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CORROSION STUDIES IN MUNICIPAL INCINERATORS

Battelle Columbus Laboratories

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CORROSION STUDIES IN MUNICIPAL INCINERATORS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SOLID WASTE RESEARCH LABORATORY

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In this field and laboratory study, corrosion probes of 11 alloys were placed in 2 municipal incinerators, one refractory lined and the other a water wall. After the probes were exposed to varying temperatures, times, and conditions, some of the conclusions included: metal-wastage rates are temperature dependent; water-wall incinerators should not be used to generate high-temperature superheated steam; hydorgen chloride and sulfur dioxide in the flue gases were of sufficient concentration to be of concern and account for the types of deposits found on the tubes; roles played by the sulfur- and chlorine-containing compounds in the refuse are of great importance and are closely interrelated; zinc and lead further complicate the corrosion process; non-metallic materials should be considered as coating for wet scrubbers of incinerator gases; corrosion of incinerator grates is not a serious problem.

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CORROSION
STUDIES
IN
MUNICIPAL
INCINERATORS

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with others from the staff of
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performed the investigation and prepared this report
for the Solid Waste Research Laboratory of the
National Environmental Research Center, Cincinnati
under Research Grants EP-00325 and EP-00325-S1

U.S. Environmental Protection Agency
Office of Research and Monitoring
National Environmental Research Center, Cincinnati

1972

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ABSTRACT

Although the water-wall incinerator permits operation of air pollution control devices and provides hot water or steam as a byproduct, there are unpredictable, severe losses of metal from the furnace tubes when these incinerators are operated.

In this ~~combined~~ field and laboratory study, corrosion probes of 11 alloys were placed in two municipal incinerators, one refractory lined and the other a water wall. After the probes were exposed to varying temperatures, times, and conditions, some of the conclusions included: ~~that the~~ metal-wastage rates are temperature dependent; ~~that~~ water-wall incinerators should not be used to generate high-temperature superheated steam; ~~that the~~ hydrogen chloride and sulfur dioxide in the flue gases were of sufficient concentrations to be of concern and account for the types of deposits found on the tubes; ~~that the~~ roles played by the sulfur- and chlorine-containing compounds in the refuse are of great importance and are closely interrelated; ~~that~~ zinc and lead further complicate the corrosion process; ~~that~~ non-metallic materials should be considered as coating for wet scrubbers of incinerator gases; ~~that~~ corrosion of incinerator grates is not a serious problem.

FOREWORD

To find, through research, the means to protect, preserve, and improve our environment, we need a focus that accents the interplay among the components of our physical environment - the air, water, and land. The missions of the National Environmental Research Centers - in Cincinnati, Ohio, Research Triangle Park, North Carolina, and Corvallis, Oregon - provide this focus. The research and monitoring activities at these centers reflect multidisciplinary approaches to environmental problems; they provide for the study of the effects of environmental contamination on man and the ecological cycle and for the search for systems that prevent contamination and recover valuable resources.

Man and his supporting envelope of air, water, and land must be protected from the multiple adverse effects of pesticides, radiation, noise, and other forms of pollution as well as poor management of solid waste. These separate pollution problems can receive interrelated solutions through the framework of our research programs - programs directed to one goal, a clean livable environment.

This study, published by the National Environmental Research Center, Cincinnati, reports on metal wastage in water-well incinerators. The increasing use of this type of incinerator makes it advisable to anticipate problems that may occur before large-scale use of these incinerators begins. Personnel on the combined field and laboratory study obtained information on deposit and corrosion problems and made recommendations on alleviating them, and they also gathered information on corrosion problems associated with wet scrubbers-- all necessary to better cope with the disposing of solid wastes in our Country.

ANDREW W. BREIDENBACH, Ph.D.
Director, National Environmental
Research Center, Cincinnati

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FIRESIDE METAL WASTAGE IN MUNICIPAL INCINERATORS
(Research Grants EP-00325 and EP-00325S1)

by

P. D. Miller, W. K. Boyd, R. B. Engdahl, R. D. Fischer,
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OBJECTIVES

The objectives of this research program are to identify the conditions that lead to fireside metal wastage in solid-waste incinerators, to determine the mechanisms by which metal loss occurs, and to devise means of preventing corrosion in these installations.

The objectives of the supplemental program are to assess the corrosiveness of the environment at incinerator grates and in scrubber chambers and to evaluate materials of construction.

INTRODUCTION

It is becoming apparent that more and more attention is being given to the use of incineration as a means of disposing of municipal refuse. This incineration must be carried out in a manner that does not create pollution problems. The use of pollution-control devices requires that the incinerator furnace gases be cooled to permit operation of the flue-gas cleaning devices. An economically attractive way in which to do this is by absorbing much of the heat by water contained in wall tubes and in convection-pass tubes used to form the furnace. Alternate procedures are to dilute the hot gases with cool air or with water. However, the latter practices greatly increase the gas volumes to be handled and thus increase the size of the pollution-control equipment.

In addition to greatly decreasing the size requirements for pollution-control equipment and fans, the water-wall incinerator has several other attractive features. First, there is a gainful use of the heat energy available in the refuse. Second, the furnace throughput can be increased because of the rapid absorption of heat possible. Third, wall slagging problems often encountered in refractory-type construction are absent.

The technology of the water-wall incinerator was developed first in Europe where it is in fairly extensive use. Corrosion problems have been reported, however, in some instances. Details of instances of severe metal wastage in incinerators along with other data on incinerator operation can be found in References (1) to (31). The first operating water-wall unit on this continent was at the Navy Public Works Center in Norfolk, Virginia, beginning in 1969. Units are now operating in Montreal, Quebec, Braintree, Massachusetts, and northwest Chicago. It is anticipated that this type of construction will become used more and more. Thus, it is important to anticipate problems which may arise before large-scale use begins.

In March, 1969, research was started at Battelle-Columbus on a grant program supported by the Solid Waste Management Office, EPA, which was aimed at determining the cause and extent of fireside metal wastage in incinerators and devising methods of alleviation. Progress on that task has been reported in detail in Annual Reports dated April 24, 1970; April 23, 1971; and April 27, 1972.

In March, 1971, work was started on a supplemental program aimed at obtaining a better understanding of incinerator-gas scrubber corrosion and also of metal wastage of grates. That work was reported in detail in the Annual Report dated April 27, 1972.

The present report draws together the research techniques used in studying the problems mentioned in the preceding paragraphs and also summarizes the conclusions reached. It covers the period March 1, 1969, through February 29, 1972.

SUMMARY

One problem faced in the operation of some European incinerators using water-cooled tubes in the walls is the unpredictably severe loss of metal from the furnace tubes. Since usage of large incinerators is increasing in the United States, it is important that the problem be understood so that techniques for its mitigation can be introduced. Of added importance are the facts that this type of incinerator is amenable to pollution control and that, at the same time, it provides hot water or steam as a by-product.

One objective of this research was to obtain information on the deposit and corrosion problems encountered in municipal incinerators which utilize waste-heat boilers and then to recommend practical and economical alleviation procedures. A second objective was to gain a better understanding of the corrosion problems associated with wet scrubbers used in pollution control for incinerators.

The research is a combined field and laboratory study. The field work has included a review of the corrosion aspects of many currently operating incinerators in this country and in Europe and, in particular, includes the use of corrosion probes inserted in operating units. These probes have been placed in a refractory-lined municipal incinerator at Miami County, Ohio, and in a water-wall incinerator operated by the Navy Public Works Center at Norfolk, Virginia. Twelve corrosion probes were exposed at Miami County and three were exposed at Norfolk. Exposure time at temperature ranged from 122 to 1318 hours. The eleven alloys listed below were used to form the individual specimens which made up the corrosion probes. Not all alloys were used on all probes.

PERFORMANCE OF ALLOYS IN FIRESIDE AREAS*

Alloy	Resistance to Wastage		
	300-600 F	600-1200 F	Moist Deposit
Incoloy 825	Good	Fair	Good
Type 446	Good	Fair	Pits
Type 310	Good	Fair	SCC**
Type 316L	Good	Fair	SCC
Type 304	Good	Fair	SCC
Type 321	Good	Fair	SCC
Inconel 600	Good	Poor	Pits
Inconel 601	Good	Poor	Pits
Type 416	Fair	Fair	Pits
A106-Grade B (Carbon Steel)	Fair	Poor	Fair
A213-Grade T11 (Carbon Steel)	Fair	Poor	Fair

* Arranged in approximate decreasing order.
** Stress-corrosion cracking.

Metal wastage rates were shown to be temperature dependent; for the carbon steels they ranged from about 10 mils per month at 325 F to about 35 mils per month at 950 F. These values, however, should not be projected to exposures of many months or years since rates decrease with extended exposure. It is estimated that rates for carbon steel tubes at about 500 F might be expected to range below about 10 mils per year for extended exposure periods.

The thermal gradients between the tube metal and the hot gases were found to be important in addition to the metal temperature.

The tabulation shows the relative performance of the eleven materials studied. As an approximation it can be assumed that "poor" is >20 mils per month, "fair" is 10-20 mils per month, and "good" is <10 mils per month. It can be seen that the Incoloy 825 gave encouraging results over the entire temperature range and is much more resistant to stress corrosion cracking than the austenitic stainless steels. The stainless types, except Type 416, lose less weight than the carbon steels at comparable temperatures, with Types 310 and 446 being superior. The major limitation for these stainless alloys is stress-corrosion cracking or pitting when in contact with moist deposits as during downtime. The Inconel 600 and 601 materials were resistant over the lower temperature region but were severely attacked at high temperatures.

While aluminum, chromium, and inorganic coatings furnished some initial protection to the tube surfaces they do not appear to be sufficiently durable to be considered for long-time boiler operation.

It is concluded that water-wall incinerators should not be used to generate high-temperature superheated steam but should be operated at relatively low metal temperatures, near 500 F, to minimize tube wastage. Steel tubes of compositions such as A106-Grade B or A213-Grade T11 can be considered at these temperatures. The Incoloy 825-type alloys would be better choices at higher temperatures.

The composition of the deposits removed from the corrosion specimens was carefully determined to provide a clue as to possible causes of the corrosion. Significant amounts of chloride, sulfur, lead, zinc, potassium and calcium, along with other more inert elements, were detected in the deposits from the two incinerators mentioned and also in incinerators at Oceanside, Long Island, and Atlanta, Georgia. Another interesting observation was that the lead content in the deposits at Norfolk and at Atlanta was unusually high.

The proportions of the various chemical compounds found on the tube surfaces depended on the probe-specimen temperature, and the distributions were consistent with known volatilities of the compounds.

Composition of the flue gas was determined at the first three sites mentioned. The HCl and SO_2 were present in sufficient concentrations (10-300 ppm) at all sites to be of concern and to account for the types of deposits found on the tubes.

X-ray-diffraction and electron-microprobe techniques were used to examine cross sections of corroded tubes and deposits. It was found with the microprobe that the elements chlorine, sulfur, lead, zinc, and potassium were concentrated adjacent to the base metal. The X-ray-diffraction studies identified over 20 compounds in the scale and deposit. Compounds of particular significance are $FeCl_2$, FeS, KCl, NaCl, $(NaK)_2SO_4$, $ZnSO_4$, $PbSO_4$, and mixed $PbO \cdot PbSO_4$ salts.

The sodium azide spot test also revealed that sulfide compounds were present near the metal surface on almost all the probe specimens, particularly on those exhibiting the most severe corrosion.

Laboratory studies were carried out at 600, 800, and 1000 F using a variety of salt compositions and under a flue-gas atmosphere containing SO_2, HCl, and, on occasion, formic acid HCOOH. The data indicate that chloride salts added to sulfate salts significantly enhance corrosion, particularly at 800 and 1000 F. The SO_2 also is an important constituent in this system. At 600 F, the most corrosive salts in decreasing order of activity were $KHSO_4$, $K_2S_2O_7$, and $ZnCl_2$. At 800 and 1000 F, $ZnCl_2$ and $PbCl_2$ were very corrosive.

Correlation of the results of the different studies made on the deposits and corroded surfaces combined with the laboratory results provide at least a tentative explanation of the corrosion mechanism. It is proposed that HCl and Cl_2 released adjacent to the tube surfaces are important factors. In addition, SO_2 and SO_3 gases, along with sulfur-containing compounds, cause additional corrosion.

The roles played by the sulfur- and chlorine-containing compounds in the refuse are of great importance and are closely interrelated.

Chloride salts reach the tube surface by direct volatilization in the flame and by reaction of the HCl formed during burning with volatilized K_2O and Na_2O. The chloride salts deposited on metal surfaces then react with SO_2 and oxygen near the tube to evolve high concentrations of HCl directly adjacent to the metal so that $FeCl_2$ is formed. Additional $FeCl_2$ is formed by reaction of iron and chlorine. The chlorine is formed when portions of the HCl are oxidized to Cl_2 is a catalyzed reaction with oxygen. This reaction is confined to areas near the metal where Fe_2O_3 is present to act as catalyst. The iron chloride in turn can decompose to form Fe_2O_3 and additional Cl_2. The iron oxide scale helps confine the system near the tube. Thus, conditions exist in which cycling between formation and decomposition of $FeCl_2$ can take place.

The other role played by sulfur is that of forming low-melting pyrosulfates or bisulfates by reaction of sulfates with the SO_3 formed near the oxide scale. These low-melting salts react directly with the steel to form FeS and additional sulfate and iron oxides.

The corrosion process is further complicated by the presence of zinc and lead salts which serve to lower the melting points of the mixtures on the metal surface.

Field studies aimed at the second objective, scrubber corrosion, have been carried out at the Montgomery County North Incinerator. Three types of stress specimens, some of them welded, were exposed in the hot water exiting from the scrubber at the incinerator. A duplicate set was exposed to the same water at a lower pH at Columbus, Ohio, under stagnant but aerated conditions. Candidate alloys for these studies were chosen primarily from those known to be fairly resistant to stress-corrosion cracking.

Pitting attack and selective attack at crevice areas constituted the major form of metal deterioration at the incinerator scrubber. At Columbus in the low pH solutions (2.0) stress-corrosion cracking was observed on Types 304 and 316L stainless steel specimens. Specimens of Inconel 600 and 601 exhibited what is termed stress-accelerated corrosion at North Montgomery County.

The alloys most resistant to all types of corrosion of those evaluated were Ti6Al-4V, Hastelloy C, Inconel 625, Hastelloy G, Hastelloy C-276, Hastelloy F, Ti75A and Type S-816.

The less-resistant alloys were Carpenter 20, Incoloy 825, Types 316L, 310 stainless steels, Inconel 600 and 601, Armco 22-13-5, USS 18-18-2, and Type 304. The following tabulation lists these 18 alloys and their general resistivity to corrosion in the scrubber solutions. The Incoloy 800 was not exposed in the scrubber water.

Evaluation of Alloys for Incinerator Scrubbers

Alloy	Corrosion Results Scrubber Solutions	Fan Deposits
Ti6Al-4V	Good resistance	Good resistance
Hastelloy C	Good	Good
Inconel 625	Good	Good
Hastelloy F	Good	--
Hastelloy C-276	Good	--
Hastelloy G	Good	--
Ti75A	Good	--
S-816	Good	Pitted
Carpenter 20	Pitted	Pitted, SCC
Incoloy 825	Pitted	Pitted
Incoloy 800	--	Pitted
316L	Pitted, SCC	Pitted, SCC
310	Pitted	--
446	Pitted	--
Inconel 600	Trenches	--
Inconel 601	Trenches	--
Armco 22-13-5	Pitted	Pitted, SCC
USS 18-18-2	Pitted	Pitted, SCC
Type 304	Pitted, SCC	Pitted, SCC

The last column in this tabulation shows eleven alloys exposed to damp deposits from the induced draft fan from N-Montgomery County. Stainless steels Types 304, 316L, USS 18-18-2, Armco 22-13-5, and Carpenter 20 were cracked to varying degrees. Pitting was noted on the alloys just mentioned as well as on Incoloy 825, Incoloy 800, and Type S-816. The most resistant alloys studied were Ti6Al-4V, Inconel 625, and Hastelloy C.

It is believed that there is merit in considering nonmetallic materials as coatings for construction of wet scrubbers for incinerator gases.

It was concluded that corrosion of incinerator grates was not a serious problem.

REVIEW OF INCINERATOR PLANT OPERATION

At the beginning of the research program in 1969, a survey was made to obtain information on the deposit and corrosion problems encountered in municipal incinerators that utilize waste-heat boilers. Installations operated by the township of Hempstead, Long Island, New York, at Oceanside and at Merrick; and by the Naval Public Works Center at Norfolk, Virginia, were visited.

The status of other incinerators in this country was determined through telephone conversations and/or correspondence. In addition, four large municipal incinerators in Europe were visited.

Corrosion at Oceanside, Merrick, and Norfolk

Severe boiler-tube corrosion was experienced at the Oceanside plant requiring replacement of many of the tubes in a 2-year period. At the Merrick plant less severe corrosion has occurred; there, the boiler has been retubed twice in its 20-year history. No corrosion problems have been encountered during the 5-year operating experience at the Norfolk plant.

Specimens of boiler-tube deposits and sections of corroded boiler tubes were obtained from the Oceanside incinerator. The deposits were found to contain from 5 to 15 weight percent lead and about 5 percent zinc in addition to the sodium, potassium, and iron ordinarily found in deposits of boilers fueled with coal or oil. From 1 to 3.5 weight percent chloride was found in different portions of the deposits, together with the usual 20 to 30 weight percent of sulfate. The presence of lead, zinc, and chloride in the incinerator deposits is the most significant difference noted to date between these deposits and those commonly encountered in coal-or oil-fired boilers. Similar observations have been reported by Bryers and Kerekes.(32) Also, it was found that hygroscopic salts were present on the Oceanside tubes; X-ray diffraction identified ferrous chloride as a major constituent of these areas.

A metallographic examination was made of corroded sections of two steel boiler tubes and one stainless steel hanger from the Oceanside incinerator. The wall thickness in some areas had been reduced from about 125 mils to 34 mils in the tube removed in 1968 and to 83 mils in the tube removed in 1969. There was nothing unusual in the microstructure of these tubes and no localized attack was evident, except the pitting as noted. Thus, the examination revealed that the tube wastage is the result of uniform corrosion. It should be noted that, while the attack is uniform in nature as opposed to selective, the wastage is more severe in some areas than in others. For example, the 4 and 8 o'clock positions generally suffered the most severe wastage. In fact, some tubes were actually perforated in other specific areas.

The stainless steel hanger was also examined at the thinnest area (0.5 in.) General surface roughening, but no selective attack, that was observed indicated that the metal wastage was the result of general attack on the hanger surface. The microstructure of this material was typical of that for an austenitic alloy. That there was no evidence of sensitization (chromium carbide precipitation at the grain boundaries) indicated that the hanger had not been above 900 F for any appreciable length of time.

Boiler Tube Reliability Experience at Other U. S. Incinerators

Only a small percentage of incinerators in the United States utilize some of their waste heat in the form of steam or hot water. Operators of the following steam generating plants were contacted by phone or in person to ascertain their experience, if any, with tube corrosion:

- Mayson Incinerator, Atlanta, Georgia
- Miami Incinerator, Miami, Florida
- Green Bay and Lincoln Incinerators, Milwaukee, Wisconsin
- Southwest Incinerator, Chicago, Illinois.

None of the above incinerator installations have had significant corrosion in their boiler units. All of them produce relatively low-pressure steam (200-300 psi) and the steam temperatures are in the range 300-400 F. In addition, the boilers are far enough from the incinerator combustion chamber so that flue-gas temperatures probably do not exceed 1000 F, as compared with temperatures up to 1900 F at Oceanside. This combination of low boiler-tube and flue-gas temperatures may account for the lack of corrosion problems at these sites.

Mayson Incinerator - Atlanta, Georgia

This waste-heat boiler following a Volund-type rotary-kiln incinerator has generated steam for outside use steadily since 1951 with no problem from corrosion. Annual revenue from steam and metal scraps is $200,000. An earlier similar plant built elsewhere in Atlanta in 1940 had given no problems. Two additional units were started up at the old plant in 1963 on the basis of the generally good experience. Steam temperature and pressure are moderate in all of these units. A later section of the present report discusses the chemical composition of the deposits from this boiler.

Miami Incinerator - Miami, Florida

Generally trouble-free experience in generating 1,500,000 pounds per day of low-pressure steam for a nearby hospital has encouraged the inclusion of waste-heat boilers for the new Miami incinerator. If there have been any corrosion failures, they have been minimal.

Lincoln and Green Bay Incinerators - Milwaukee, Wisconsin

Generation of building heat and hot water in waste-heat boilers at the Lincoln and Green Bay incinerators has been free of corrosion difficulties.

Southwest Incinerator - Chicago, Illinois

The waste-heat boilers following the rotary-kiln-type incinerators at this plant have been generating steam for outside use since 1963 without serious difficulty from tube corrosion.

Corrosion at Mannheim, Stuttgart, Munich, and Rotterdam

Travel to England in November, 1969, for Battelle on other matters afforded an opportunity to visit four large municipal incinerators in Germany and Holland. The four installations visited were selected because all had reported corrosion problems. The four installations were remarkably similar on many counts; however, comments from the operators about possible causes of metal wastage differed considerably.

Prior to these plant visits, a day was spent at Battelle's Frankfurt Laboratories reviewing the corrosion problem in incinerators. That discussion pointed out the fact that no one in Europe really understands the cause of the corrosion. The explanations advanced are based on surmise rather than on facts, and many analyses have been made of the deposits in corroded areas.

Conclusions from these European visits are as follows:

- Corrosion occurs to some degree in all large municipal heat-recovery incinerators, to an extent and under conditions still generally unknown.
- Attempts in the past to describe the mechanism of the attack have been based mainly on supposition, using basic premises and similarity with other systems. More recent studies have aided greatly in providing a better understanding of the processes involved.
- Probes have been placed in some incinerators, but no worthwhile data have been obtained from them, apparently because no serious attempts were made to interpret data from the deposits formed on the probes.
- The evidence regarding the role of lead and zinc in the corrosion is sparse.
- Erosion is blamed for much loss of metal, generally on the supposition that products of corrosion removed from the metal surface by erosion expose fresh metal to oxidation.
- Temperature is considered an important factor, with some agreement that a maximum metal temperature of about 600 F should not be exceeded. Nevertheless, steam temperature as high as 1000 F is not uncommon.
- Corrosion is often attributed to "flames", based on the observation that corrosion is found in wall areas where flames are present.

- Alternate oxidation and reduction caused by intermittent flame contact is the cause of corrosion, according to some workers, on the basis that Fe_2O_3 reacts with HCl under reducing conditions to form $FeCl_2$, which then converts to the oxides under oxidizing conditions. An alternative proposal is that iron is converted to $FeCl_2$, which changes to $FeCl_3$ at slightly higher temperatures.

- Chlorine from plastics such as polyvinylchloride is blamed only in part for corrosion, in the belief that much larger quantities than 2 percent of the refuse will be necessary before PVC becomes troublesome.

- Refuse is used to produce electricity, but the quantity is small, and the efficiency of conversion is low. Such plants are mostly used in conjunction with an existing power plant of much greater capacity.

- Municipal refuse can be burned in combination with other fuels, such as pulverized coal or residual fuel oil, in a variety of furnaces. Many different configurations have operated successfully.

- Large amounts of sulfates are found in most deposits in corroded areas, but the pH of a water solution of such deposits generally is not low. Apparently, the sulfates could be connected with fillers used in paper, such as $CaSO_4$.

- Combustion conditions are unbelievably bad in large municipal incinerators burning raw garbage. Martin grates, Dusseldorf grates, and conventional chain-grate stokers all have large masses of cold refuse in proximity to burning zones. That the final material dumped from the end of the combustor contains so little unburned material is remarkable. Agitation within the fuel bed in a Martin stoker is generally considered beneficial to complete combustion.

- Relatively large amounts of material burn in suspension (mainly bits of paper), because of the very high velocity of the primary air through holes in the fuel bed where combustion is occurring at a high rate.

FIELD STUDIES OF INCINERATOR FIRESIDE CORROSION

Corrosion-Probe Studies

In order to obtain realistic estimates of tube wastage and deposit formation, it was necessary to perate probes in the field over extended periods.

The field studies conducted on this program have included:

(1) Installation of corrosion probes in the municipal incinerator operated by Miami County, Ohio and in the Salvage Fuel Boiler operated by the Navy at Norfolk, Virginia.

(2) Sampling of flue gas at the Miami County, Ohio, the Oceanside, Long Island, and the Norfolk incinerators.

(3) Analysis of the boiler-tube deposits from the Oceanside incinerator, the Atlanta Mayson incinerator, and those built up on the corrosion probes in the Miami County, Ohio, and the Norfolk, Virginia, incinerators.

Design and Construction

The probe was designed to include 34 cylindrical specimens nested together end to end and then inserted into the incinerator through a side wall. The section of the probe extending through the wall was water cooled. The specimens exposed within the furnace were cooled by air flowing inside the tubular specimens. A computer analysis was used to ascertain the geometry of the internal support tube required to give the most linear specimen-temperature variation over the range of about 350 to 1100 F for a probe with 34 specimens. Each specimen was about 1.25 inches in OD, 1.00 inch in ID, and 1.5 inches long. Figure 1 shows an assembled probe positioned with the hot specimen end down and the water-cooled end up. The corrosion specimens begin at the transition point just above the left hand of the man holding the probe. The probe is placed in a horizontal position in the incinerator.

The appearance of individual specimens is illustrated in Figure 2, which shows a probe being assembled. The four holes visible on the hot-end closure section are passageways for the exit of the cooling air. Figure 3 is a schematic of the final exposure-probe apparatus. The specimens are nested together with lap joints as shown in Detail A and are retained axially at the cooling-air-outlet end by a retainer which is fixed to the internal support tube with webs as shown in Section A-A. The axial restraining force in the internal support tube is obtained by compressing the spring on the air-inlet end of the probe at assembly. Also, the spring compensates for diffential thermal expansion between the specimens and the internal support tube.

Specimen temperatures are measured at four stations with Type K thermocouples either welded into the wall of the specimens or inserted into recesses drilled lengthwise into one end of the appropriate specimen.

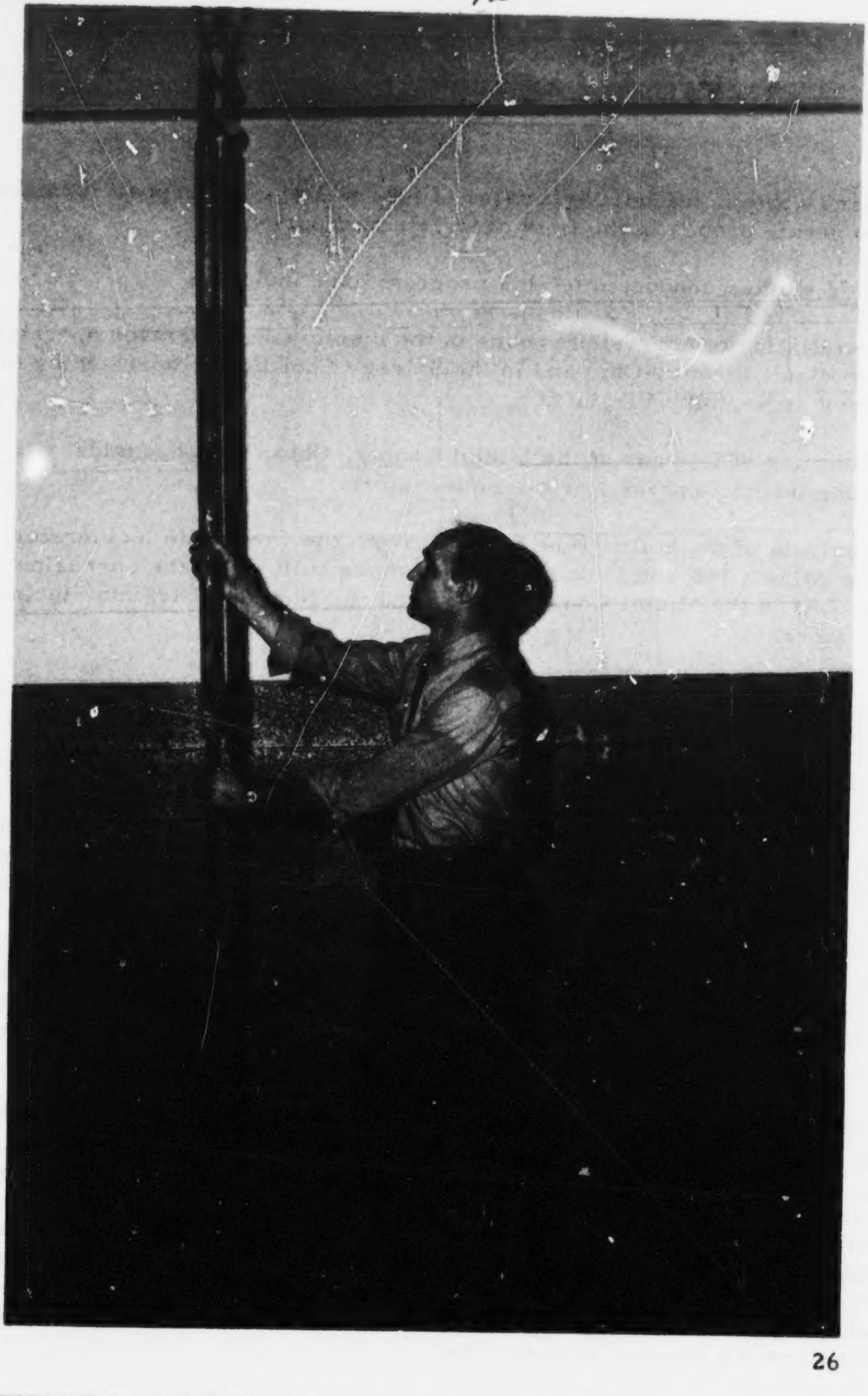

FIGURE 1. CORROSION PROBE AFTER REMOVAL OF DEPOSIT

Cold end at top. Specimens begin just above the left hand of the operator and extend downward.

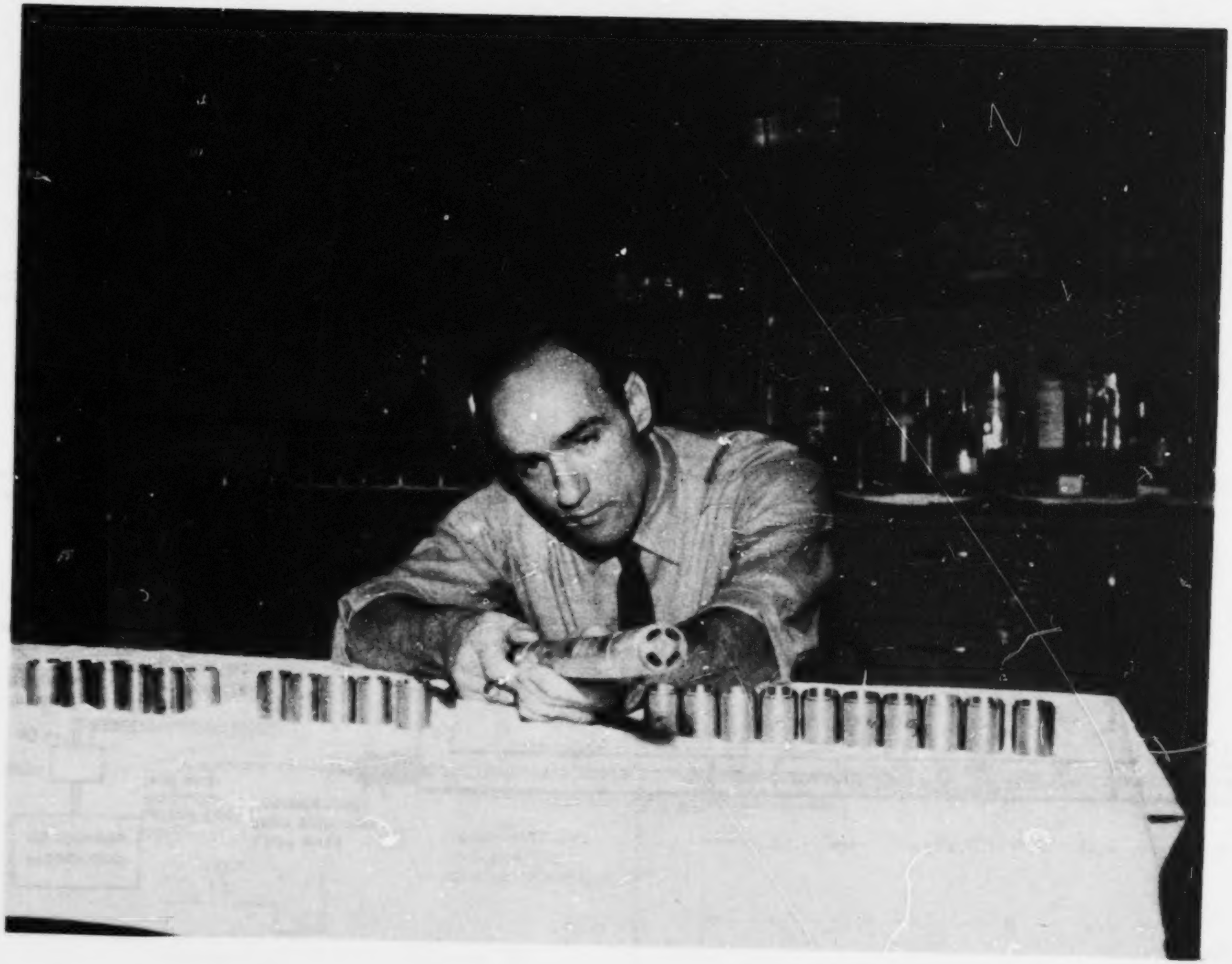

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FIGURE 2. SPECIMENS BEING ASSEMBLED TO FORM CORROSION PROBE

The air exit vents are visible at the hot end of the probe.

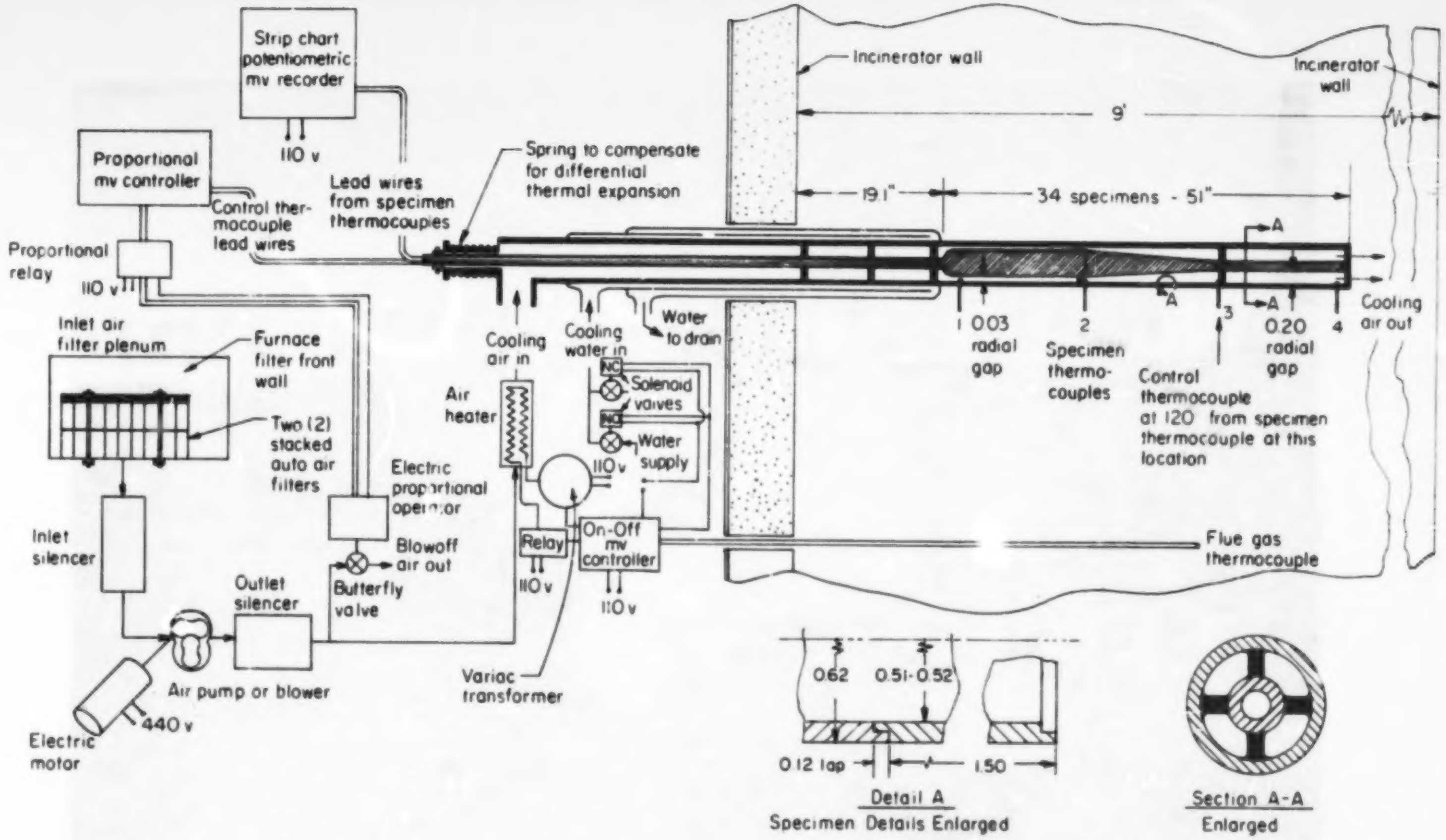

Strip chart potentiometric mv recorder
110 v
Proportional mv controller
Control thermocouple lead wires
Lead wires from specimen thermocouples
Spring to compensate for differential thermal expansion
Proportional relay
110 v
Inlet air filter plenum
Furnace filter front wall
Two (2) stacked auto air filters
Inlet silencer
Electric motor
440 v
Air pump or blower
Outlet silencer
Electric proportional operator
Blowoff air out
Butterfly valve
Cooling air in
Air heater
Relay
110 v
Variac transformer
Cooling water in
NC
Solenoid valves
NO
Water supply
110 v
On-Off mv controller
110 v
Water to drain
Incinerator wall
9'
19.1"
34 specimens - 51"
Incinerator wall
A
A
A
1 0.03 radial gap
2 Specimen thermocouples
3
Control thermocouple at 120 from specimen thermocouple at this location
0.20 radial gap
4
Cooling air out
Flue gas thermocouple
0.62
0.51-0.52
0.12 lap
1.50
Detail A
Specimen Details Enlarged
Section A-A
Enlarged

FIGURE 3. SCHEMATIC OF SPECIMEN-EXPOSURE-PROBE APPARATUS

The thermocouple lead wires are brought out of the probe through the center of the internal support tube, so that temperatures can be recorded continuously on a strip-chart potentiometer recorder. Since the computer results indicated that the temperature variation is linear for regions with a constant gap between the internal support tube and the specimens, the four temperatures accurately define the specimen temperatures.

The specimen temperatures are controlled by regulating the amount of cooling air admitted to the probe. The output from a control thermocouple, which is attached to the specimen at the same axial location as the Thermocouple 3, is monitored by a proportional temperature controller. At the start of a test, the controller setpoint is adjusted to maintain either the lowest temperature at Thermocouple 1 or the highest temperature at Thermocouple 4, depending on the test objective. The controller maintains this temperature by varying the amount of cooling air bypassing the probe through a motorized butterfly valve located between the blower and the probe. A Roots-blower air pump delivering up to about 34 cfm was used with a 5-hp motor as a drive.

Specimens

Eleven different metals and alloys and five different types of coating were evaluated in the field probe studies. Carbon steels A106-Grade B and A213-T11, a low-alloy Cr-Mo steel, were used in the lower temperature regions, i.e., not over 1000 F. Types 304, 310, 316, 321, 416, and 446 stainless steels were exposed primarily at the higher temperature regions but some were exposed at lower temperatures to provide a direct comparision with the carbon-steels. The nickel-base alloys, Inconel 600, Inconel 601, and Incoloy 825 were also used to form specimens for use at several locations over the length of the probe.

The nominal compositions of these alloys is given in Table 1. This table also includes the composition of additional alloys which were evaluated in the wet scrubber as discussed in later sections of this report. As can be seen in the table, some alloys were evaluated in both fireside areas and in the scrubber.

Specimens protected with several types of coatings were included in the fireside probe studies. One set was coated by Superchrome Plating and Engineering Company, Inc., with about 5 mils of hard chromium. Such coatings had provided protection to superheater tube areas in oil-fired power stations. A second set was coated by Armco Steel Corporation with aluminized Type 1 coating to a thickness of about 2 mils. Such aluminized coatings have proved useful in flue gas or exhaust gas atmospheres. Three types of inorganic coatings (cermets) were also evaluated. The inorganic coatings (W, 570W, and 570+W) were applied by the Sermetel Division of Teleflex, Inc., and represented types used to protect turbine blades during high-temperature operation. These coatings were applied to A106 and T-11 steel specimens.

Operation in Incinerators

The helpful and cooperative managements of the incinerator at Miami County, Ohio, and at the Navy Public Works Center at Norfolk, Virginia, permitted insertion of the probes in two routinely operating incinerators. The program at Miami County began early in December, 1969. Since two self-sufficient probe assemblies were constructed, it was possible to operate at Norfolk, Virginia, concurrent with operation at Miami County. The work at Norfolk began in August, 1970. Table 2 shows the exposure

TABLE 1. NOMINAL COMPOSITION OF ALLOYS USED IN FIRESIDE AND SCRUBBER STUDIES

Alloy	Fireside Probe	Scrubber	Cr	Ni	Mo	Fe	Si	W	Cu	Al	Co	Mn	C
Type 446	Yes	Yes	26.5	0.5 (max)	--	Bal	0.75 (max)	--	--	--	--	1.5	0.2
Type 310	Yes	Yes	25	20.5	--	Bal	0.75 (max)	--	--	--	--	2.0	0.15
Inconel 601	Yes	Yes	23	60.5	--	14.1	0.25	--	0.25	1.4	--	0.5	0.05
Hastelloy F	No	Yes	22	45	6.0	21.0	1.0	1.0	--	--	2.5	1.5	--
Hastelloy G	No	Yes	22	45	6.5	20.0	--	--	2.0	--	--	1.5	0.05 Cb+Ta 2.0
Armco 22-13-5	No	Yes	22	13	2.0	Bal	1.0	--	--	--	--	5.0	0.06 (max
Inconel 625	No	Yes	21.5	61	9.0	2.5	0.25	--	--	0.2	--	0.25	0.05 Cb+Ta 3.65
Incoloy 825	Yes	Yes	21.5	42.0	3.0	30.0	0.25	--	2.25	0.1	--	0.5	0.03 Ti 0.9
Incoloy 800	No	Yes	21	32.5	--	46.0	0.5	--	0.4	0.4	--	0.75	0.05
Carpenter 20	No	Yes	20	29.0	2.0	43.6	1.0	--	3.0	--	--	--	--
Type 304	Yes	Yes	19	9.5	--	Bal	0.75 (max)	--	--	--	--	2.0 (max)	0.08
Type 321	Yes	No	19	11	--	Bal	0.75 (max)	--	--	--	--	2.0 (max)	0.08 Ti5XC
S816	No	Yes	19	20	4	3	--	4	--	--	45	--	4Cb
USS 18-18-2	No	Yes	18	18	--	Bal	2	--	--	--	--	--	--
Type 316 L	Yes	Yes	17	12.5	2-3	Bal	0.75 (max)	--	--	--	2	--	0.03
Hastelloy C	No	Yes	15.5	56	16	5.5	1	4	--	--	--	1.0	0.08
Hastelloy C-276	No	Yes	15	56.5	16	5.5	Low	4.5	--	--	2 (max)	1	Low
Inconel 600	Yes	Yes	15.5	76	--	8	0.25	--	0.26	--	--	0.5	0.09
Type 416	Yes	No	13	--	--	Bal	1	--	--	--	--	1	0.15
A213 Grade T11	Yes	No	1.25	--	0.5	Bal	0.75	--	--	--	--	0.4	0.15
A106 Grade B	Yes	No	--	--	--	Bal	0.1	--	--	--	--	0.8	0.3
Titanium 75A	No	Yes	--	--	--	--	--	--	--	--	--	--	--
Titanium 6Al4V	No	Yes	--	--	--	--	--	--	--	--	--	--	--

Trade names of materials are used in this report to illustrate types and classes; results are not to be taken as an endorsement of any product.

TABLE 2. CORROSION-PROBE EXPOSURE SCHEDULE

Probe	Site	Gas Temp, F	Time Interval	Total Time in Furnace, hr	Time at Temp, hr	Heated During Downtime
1	Miami County	1200-1500	Dec. 2 - Dec. 23, 1969	506	312	No
2	Miami County	1200-1500	Jan. 21 - March 2, 1970	893	389	Yes
3	Miami County	1200-1500	March 2 - March 30, 1970	666	323	No
4	Miami County	1200-1500	April 21 - April 30, 1970	219	122	Yes
5	Miami County	1800-2200	May 15 - June 1, 1970	411	190	Yes
6	Miami County	1200-1500	July 7 - July 24, 1970	412	218	No
7	Miami County	1800-2200	July 20-July 28, 1970	188	101	Yes
8	Norfolk	1000-1200	Aug. 11 - Aug. 28, 1970	240	180	No
9	Miami County	1200-1500	Oct. 21 - Jan. 4, 1971	1820	828	No
10	Norfolk	900-1100	Sept. 14 - Oct. 2, 1970	227	188	No
11	Norfolk	1000-1200	Dec. 14 - March, 19, 1971	2304	1318	No
12	Miami County	1200-1500	June 6 - July 10, 1971	816	492	No
13	Miami County	1200-1500	Aug. 24 - Sept. 8, 1971	356	206	No
14	Miami County	1200-2000	Oct. 12 - Nov. 14, 1971	792	420	No
15	Miami County	1200-1700	Dec. 12, 1971 - Jan. 4, 1972	576	291	No

schedule for each of these incinerators. It will be noted that the total time in the furnace was usually much longer than the time at temperature. Operation at Miami County usually was for 4 to 5 days a week; at Norfolk, the two furnaces were operated alternately 1 week at a time.

As can be seen in Figure 3, the probe assembly was designed to provide heating to prevent condensation from the atmosphere during downtime. Table 2 indicates the runs where this equipment was used (Runs 2, 4, 5, and 7).

Miami County, Ohio. The corrosion probes for Runs 1, 2, 3, 4, 6, 9, 12, 13, 14, and 15 were installed in the Miami County Incinerator's furnace-outlet sampling port located over the last half of the bridge wall, as shown in Figure 4, Location 1. This sketch shows the incinerator arrangement relative to the sampling port. In this location, the corrosion specimens are exposed to radiation from the flame and they in turn radiate to the cooler downstream scrubber. Seldom, if ever, did flame from burning refuse reach the probe; most of the heat transfer to the tube probably was by convection. In some cases, pieces of burning refuse carried by the flue-gas streams and burning in suspension may deposit on the probe and cause local high temperatures.

No special firing of the incinerator was done for this study. The 150-ton-per-24-hour-day incinerator operated around the clock on a 4 to 5-day-week schedule. Burning rates were governed by such factors as the type of refuse received and the moisture content of the refuse. While the incinerator was being fired, the flue-gas temperature at the location of the corrosion probe normally ranged between 1200 F and 1500 F. During furnace-shutdown periods over weekends or during breakdowns, the temperature in the incinerator dropped below 200 F. Because moisture is usually present in the scrubber system, humidity in the incinerator during shutdown could be quite high. As mentioned before, provision was made in some tests to keep the probe warm during this period.

The corrosion probes for Runs 5 and 7 were installed at Location 2 in the same incinerator. This is directly in the flame area, so that temperatures on occasion reached 2000 F.

Norfolk, Virginia. Corrosion probes for Runs 8, 10, and 11 were installed in one of the two units of the Salvage Fuel Boiler (incinerator) operated by the Navy Public Works Center at Norfolk, Virginia. Each furnace can burn 150 tons of refuse per day. The walls of each furnace, including the main uptake to the convection boiler, are water cooled. The water walls radiantly heated are 2-1/2-inch diameter on 3-1/4-inch centers. The upper convection section of the boiler consists of 2-1/2-inch-diameter tubes on 7-inch centers in a conventional two-drum design.

Figure 5, taken from a paper by Moore(9), shows the layout of this unit and the location of the corrosion probes. Probes 8 and 11 were located at the lower position shown in the convection passes of the boiler. Probe 10 was located about 8 feet higher up in the same general area. Gas temperatures in these areas were in the range 1000 to 1200 F at the lower location and in the range 900 to 1100 F at the upper location.

The main difference in the type of refuse fired at Norfolk as compared with that at Miami County was a greater content of wood and smaller amounts of tin cans. However, the refuse does contain rather large pieces of scrap metal. The refuse at Norfolk, which is collected from Naval activities and ships, include paper products, crates and packing materials, plastics, and garbage, as well as the noncombustible materials such as metal

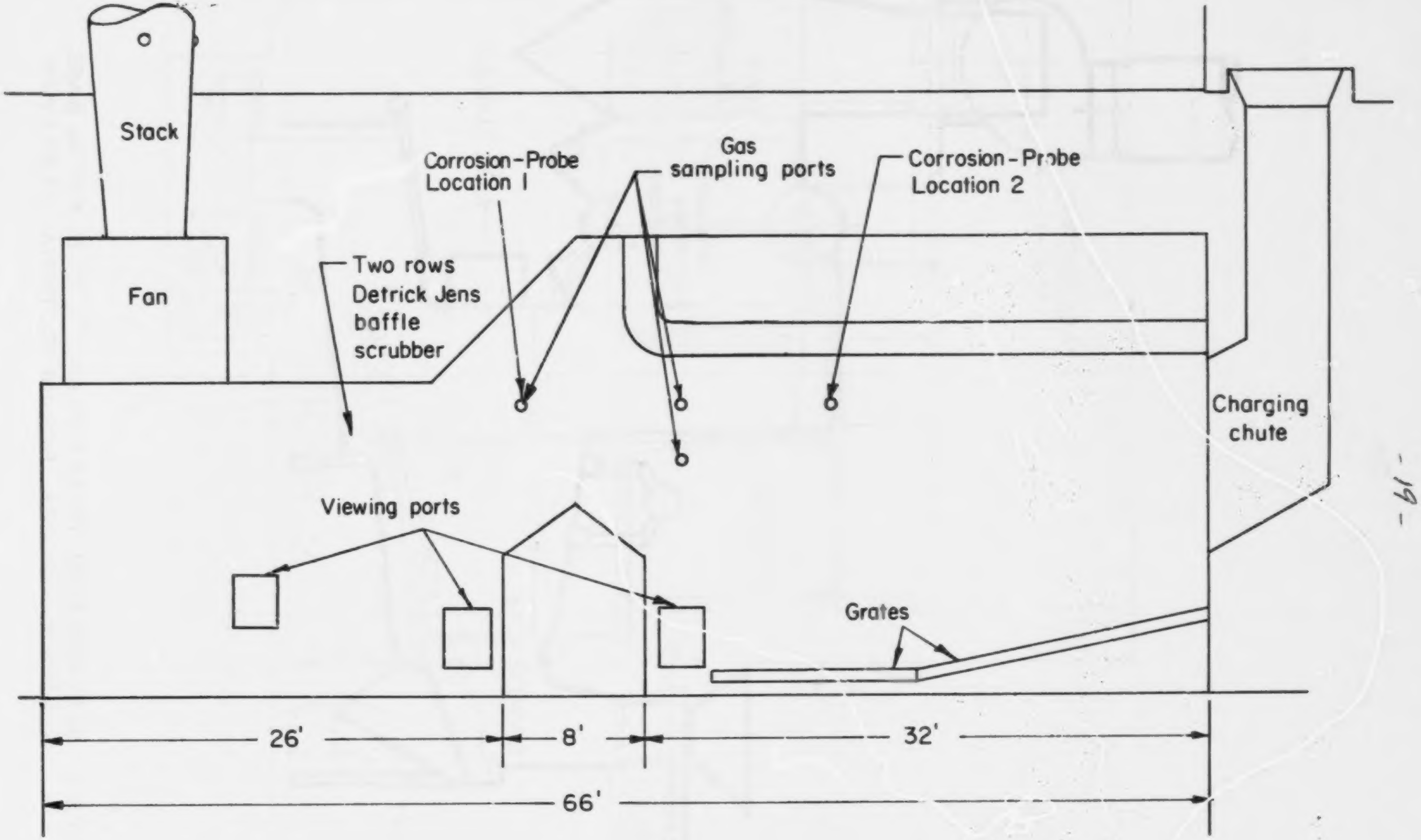

Stack
Fan
Two rows Detrick Jens baffle scrubber
Corrosion-Probe Location 1
Gas sampling ports
Corrosion-Probe Location 2
Charging chute
Viewing ports
Grates
26'
8'
32'
66'

FIGURE 4. SKETCH OF MIAMI INCINERATOR

Scale: 1/8-inch = 1 foot.

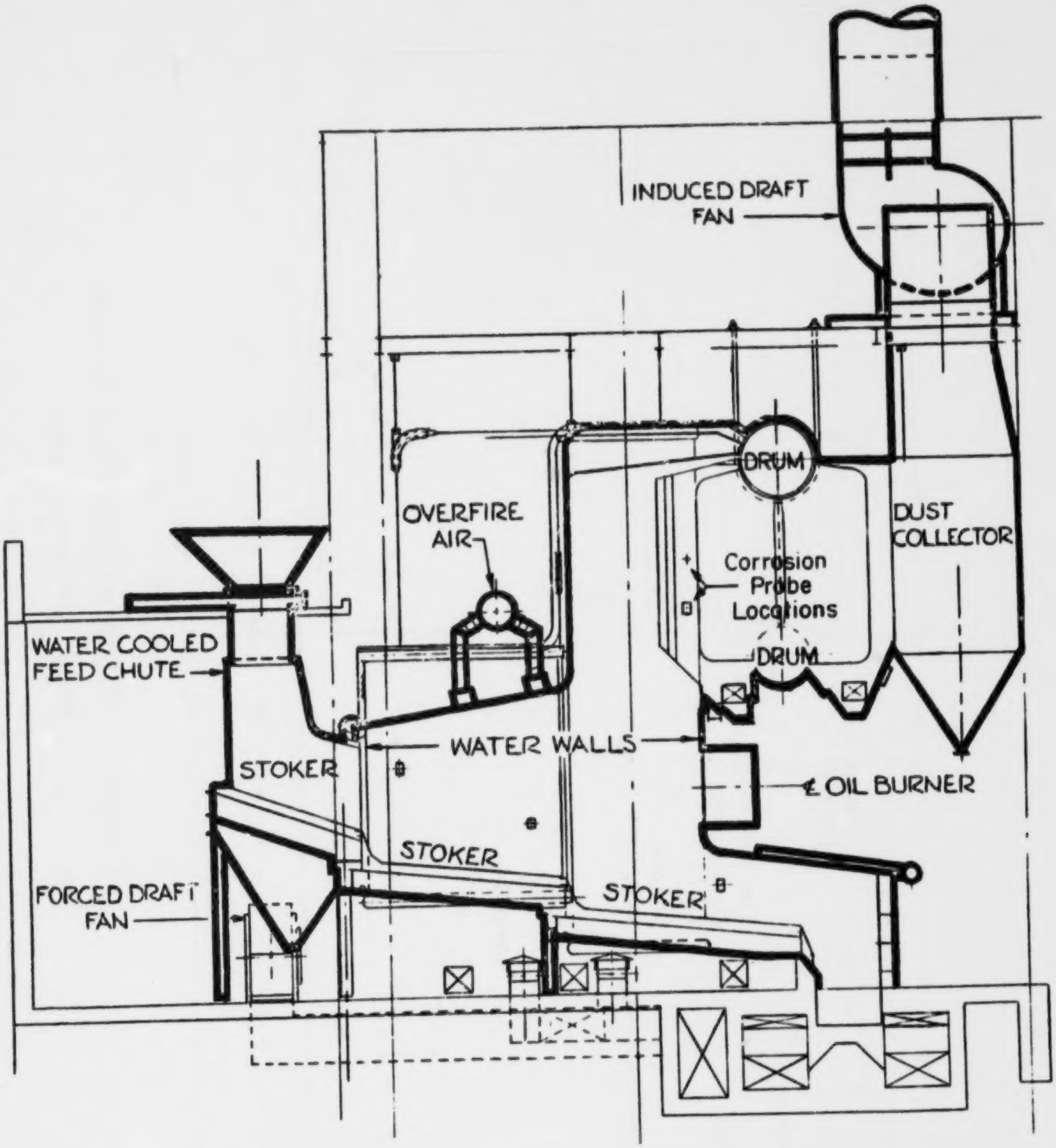

INDUCED DRAFT FAN
DRUM
OVERFIRE AIR
DUST COLLECTOR
Corrosion Probe Locations
DRUM
WATER COOLED FEED CHUTE
WATER WALLS
STOKER
℄ OIL BURNER
STOKER
FORCED DRAFT FAN
STOKER

FIGURE 5. SALVAGE FUEL BOILER PLANT(9), U. S. NAVAL BASE, NORFOLK, VIRGINIA, BOILER SECTIONAL ELEVATION

and glass. Observations also suggest that the amount of PVC plastic in the Norfolk refuse is less than that at a municipal incinerator such as the one at Miami County.

FIELD CORROSION RESULTS

Procedures

The corrosion probes as removed from the incinerators are covered with scale and deposits. More of these deposits were found at Miami County than at Norfolk. The deposit built up into a V-shaped layer of varying depth lengthwise along the probe, with the apex or point of the V projected into the oncoming gas stream. The appearance of Probe 9 after removal from the incinerator at Miami County is shown in Figure 6. The high-temperature end of the probe is to the right of the photograph and is being raised by the man shown in the picture.

It can be seen that the deposit in this area is about 4 inches thick. Another even thicker deposit is evident on the water-cooled section of the probe as shown to the left in the photograph.

These deposits were removed from all probes in a numbered sequence. Thus, the variations in composition as a function of temperature could be determined when the deposits were analyzed.

Frequently, and particularly on the carbon steel, an "egg-shell" scale was formed directly adjacent to the base metal and below the deposit. This scale, which was magnetic, was sometimes 10 to 20 mils thick and was discolored blue-black. The appearance of this scale and deposit can be seen in Figure 7. Note that the deposit builds up in contoured striated layers. The deposit, which was about 3/4 inch thick in this case, came from Probe 4 near Specimens 16 and 17. The corrosion specimens shown in this photograph have been descaled chemically.

Individual specimens were separated and examined. They were tested first for the presence of sulfide by placing a drop of sodium azide solution (33) on the surface and viewing the reagent under a binocular microscope. Evolution of nitrogen gas bubbles gave a positive identification of sulfide. Another area was then checked for pH by placing a moistened strip of Universal pH paper over the surface. Thus, the hydrolytic properties of salts present on the surfaces could be determined.

Selected specimens were retained intact for special examination by X-ray, electron-microprobe, and metallographic procedures.

The other pieces were then descaled by methods which prevented attack of the base metal. Details of the stripping procedures are given in the Appendix. The amount of metal wastage was determined by weight-loss measurements.

On the basis of OD and ID micrometer measurements, the overall weight loss was adjusted to reflect the proportion of loss which occurred on the outside surface. This was of significance only in the cases where appreciable oxidation had occurred on the inner surfaces. The wastage rates for the specimens were calculated and expressed as

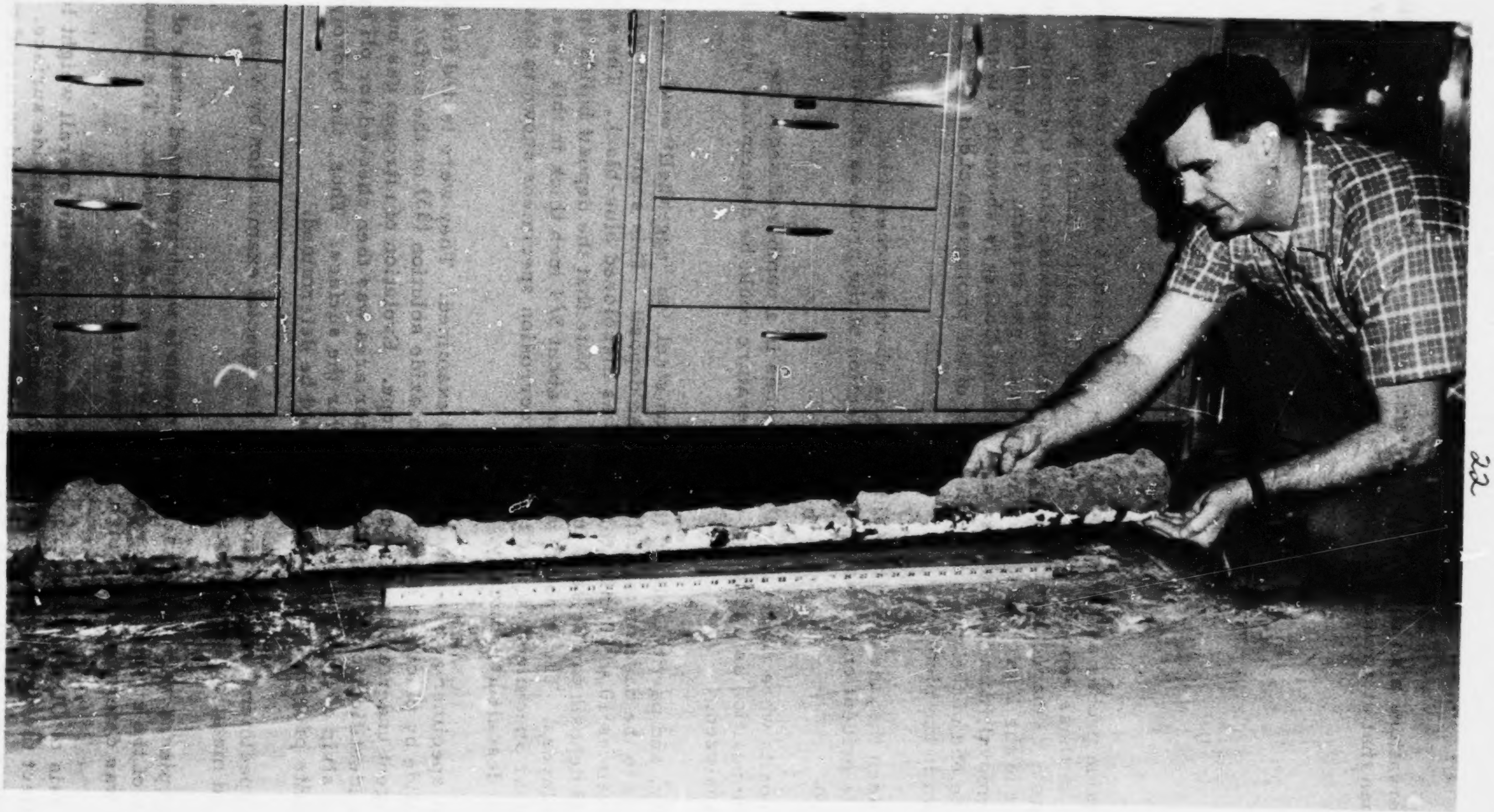


FIGURE 6. PROBE 9 FROM INCINERATOR AT MIAMI COUNTY SHOWING DEPOSIT

The water-cooled section of the probe is to the left in the photograph.

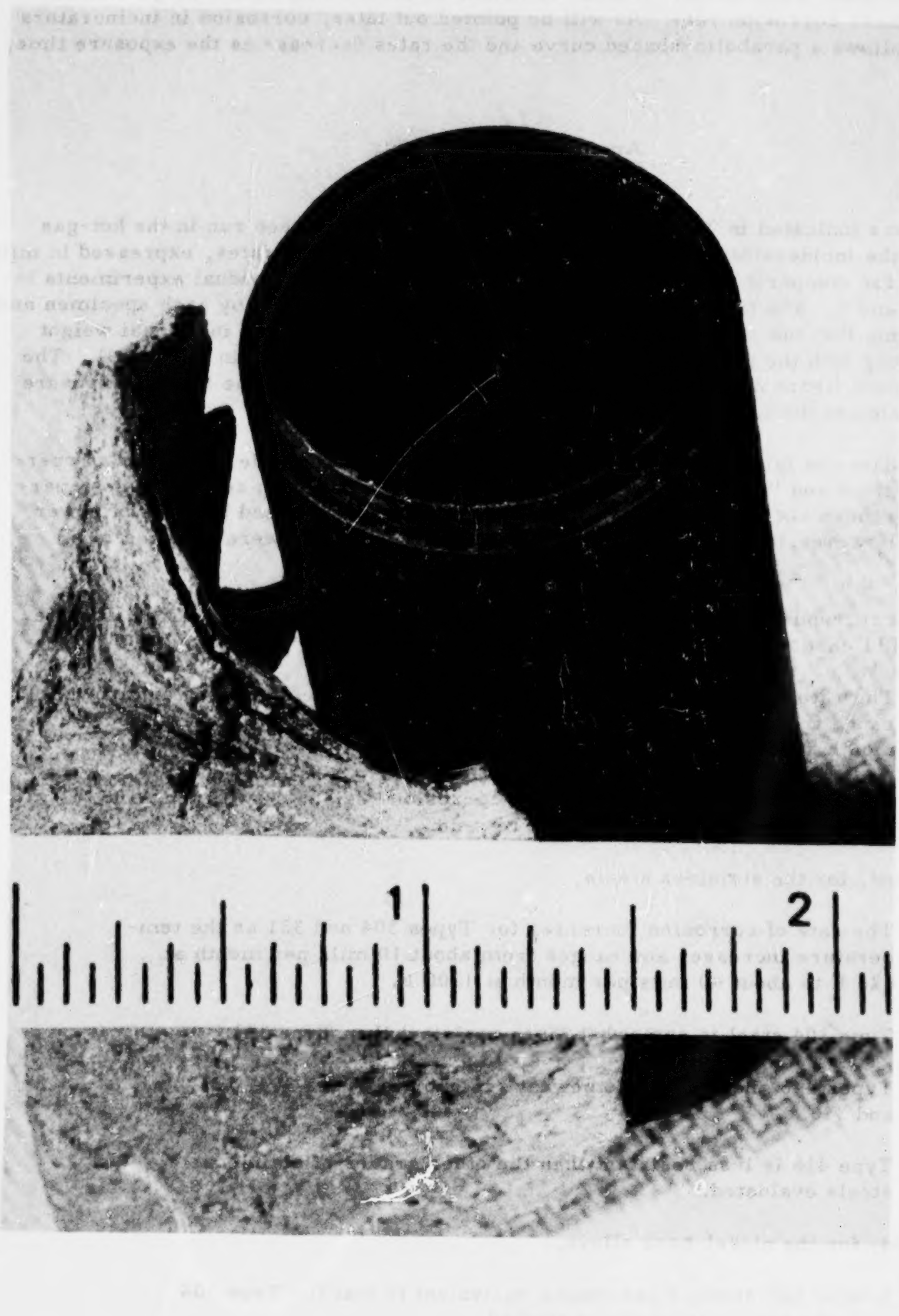


FIGURE 7. DEPOSIT AND SCALE AS REMOVED FROM SPECIMENS 16 AND 17 OF PROBE 4

The metal-tube specimens shown have been descaled.

"mils per month" penetration. It must be noted, however, that such a projection assumes a linear corrosion rate. As will be pointed out later, corrosion in incinerators probably follows a parabolic-shaped curve and the rates decrease as the exposure time increases.

Area 1 at Miami County

As was indicated in Table 2, ten corrosion probes have been run in the hot-gas section of the incinerator at Miami County. The metal-wastage rates, expressed in mils per month for comparison purposes, are summarized for the individual experiments in Figures 8 and 9. The figures also show the temperatures reached by each specimen and the total time that the specimen was at temperature. Details of the individual weight losses, along with the penetration rates, are given in the Appendix in Table A-1. The graphs in each figure have been arranged with those representing the longest exposure period located at the top of the page and the shortest at the bottom.

The data are fairly consistent considering that there are wide variations in operating conditions and "fuel". Some overheating was experienced in several cases, particularly in those shown in Figure 9, because of blower outages and because of power failures. However, meaningful comparisons between materials were obtained in all cases.

Several trends of importance can be seen in the ten bar graphs. First, for the A106 and T11 carbon steels,

- The rate of corrosion increases as the temperature increases and can range from 5 to 15 mils per month at 325 F to about 20 to 50 mils per month at 950 F.
- The two steels are comparable in corrosion resistance with the A106 being slightly superior to the T11 grade.

Second, for the stainless steels,

- The rate of corrosion increases for Types 304 and 321 as the temperature increases and ranges from about 10 mils per month at 625 F to about 40 mils per month at 1200 F.
- Type 304 steel is somewhat more resistant then Type 321.
- Types 446 and 310 are somewhat superior to Types 304, 321, and 316.
- Type 416 is less resistant than the other grades of stainless steels evaluated.

Third, for the nickel-base alloys,

- Incoloy 825 shows a resistance equivalent to that for Type 304 over the temperature range studied.

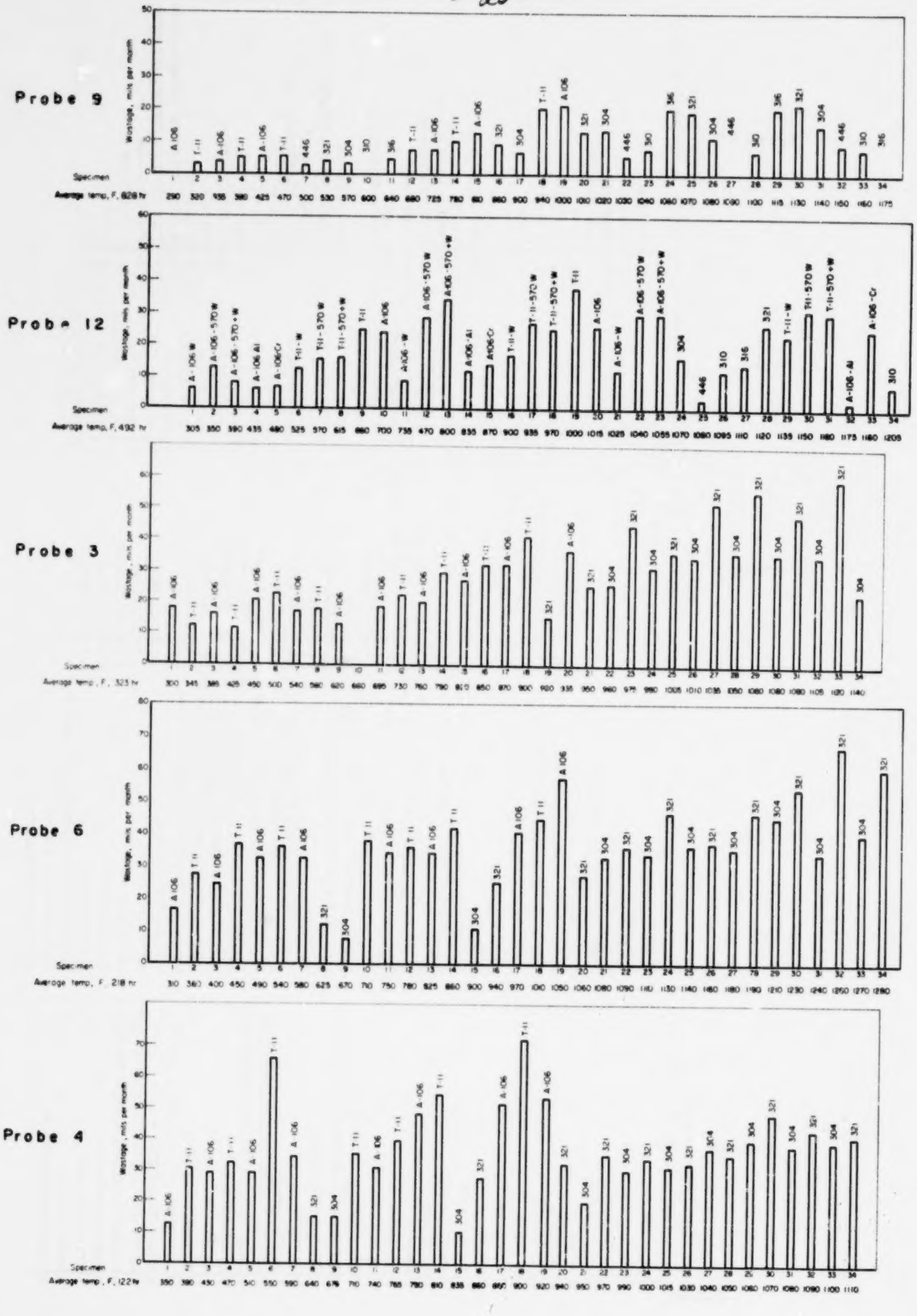


FIGURE 8. TUBE WASTAGE RATES FOR PROBES EXPOSED AT MIAMI COUNTY

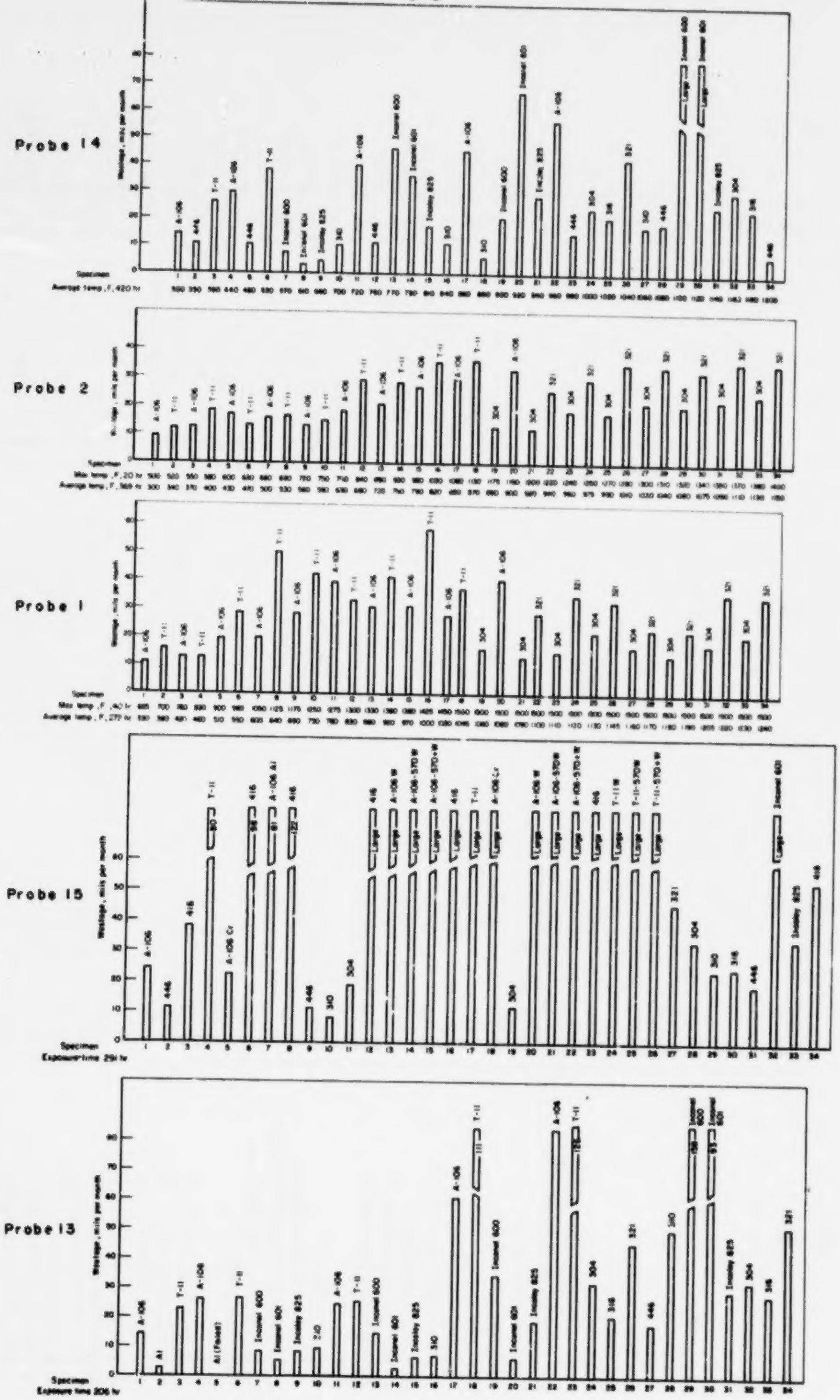


FIGURE 9. TUBE WASTAGE RATES FOR PROBES EXPOSED AT MIAMI COUNTY

- Inconel 600 and 601 have poor resistance in the high-temperature regions, i. e. , above about 800 F.

Fourth, for protective coatings,

- Metallic coatings of aluminum and chromium furnish short-time protection but are not durable during long exposures.

- Inorganic ceramic type coatings do not show long-time protective action.

Fifth, heating during downtime showed no significant effect (see Probes 2 and 4). As will be discussed later, however, the downtime conditions may lead to stress-corrosion cracking of the stainless steels.

Comparison of the results from six probes when arranged according to the time of exposure shows that the initial corrosion rates are high and that they taper off with time. Such a comparison for the A106 carbon steels is illustrated in Figure 10, where the specimen numbers are plotted as a function of wastage and exposure time. The approximate temperatures are indicated by a lower band near 400 F extending to an upper band of 850 F. It can be seen that the wastage rates range from about 3 to 12 mils per month at 828 hours to about 30 to 55 mils per month at 120 hours.

The results suggest that the scale formed during corrosion is protective to some extent and that the rate of attack will decrease appreciably as the exposure time is increased. German experience as reported by Eberhardt and Mayer(16) agrees with this observation. Hilsheimer(2) also points out that cleaning the tubes increases the rate of corrosion. Some cleaning, most likely with soot blowers, will be required to maintain good heat transfer, but the optimum frequency of cleaning is not known at present.

The present data are not precise enough to permit an exact extrapolation of wastage rates to exposures of many months or years, but some idea of the magnitude can be obtained from Figure 10.

Metallographic studies of sections from specimens of the A106 and T11 carbon-steel alloys indicated that the attack was uniform. Stainless steel specimens on the other hand showed some structural changes and varying degrees of intergranular attack.

General observations on all specimens from all probes indicate that somewhat greater wastage occurs in the area away from the point of maximum thickness of the deposit. If the maximum deposit and wall thickness are considered to be at the 12 o'clock position, the minimum wall thickness often occurs around the 6 o'clock position.

Area 2 at Miami County

Two corrosion probes were exposed in the flame area in the incinerator at Miami County. Because of the high temperature here, the hot end of the probe reached about 1500 F even after the probe had been shortened to include only 19 specimens as compared with the 34 normally used. As can be seen in Figure 11 for Probes 5 and 7, respectively, the lowest specimen temperature reached was about 460 F. This figure also shows the wastage rates experienced for the two probes. Detailed results are given in

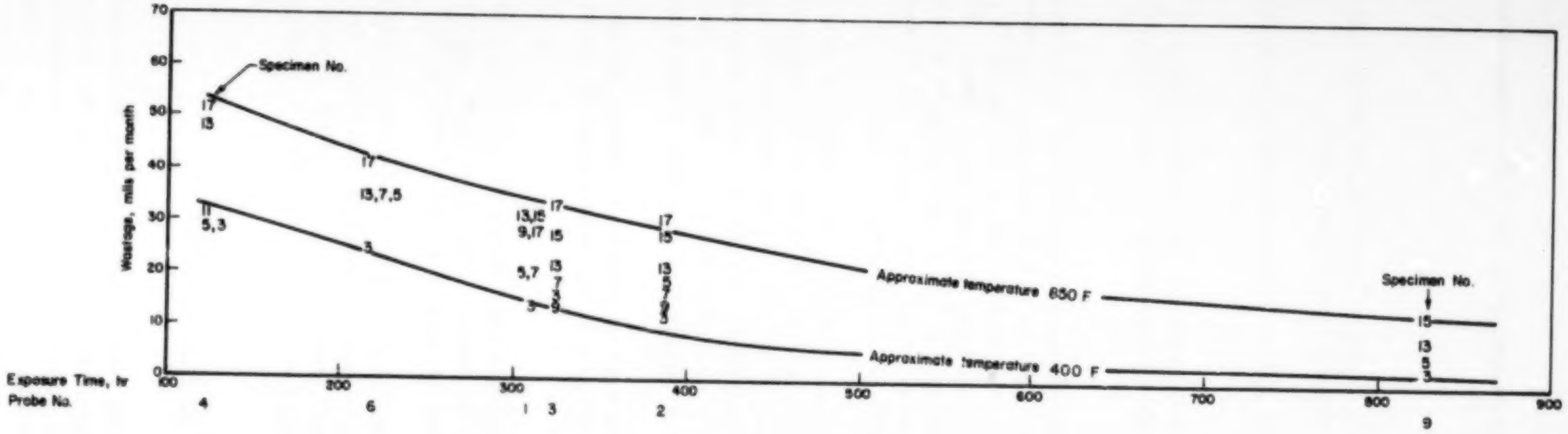


FIGURE 10. METAL WASTAGE AS A FUNCTION OF EXPOSURE TIME

These probes were exposed at Position 1, Miami County.

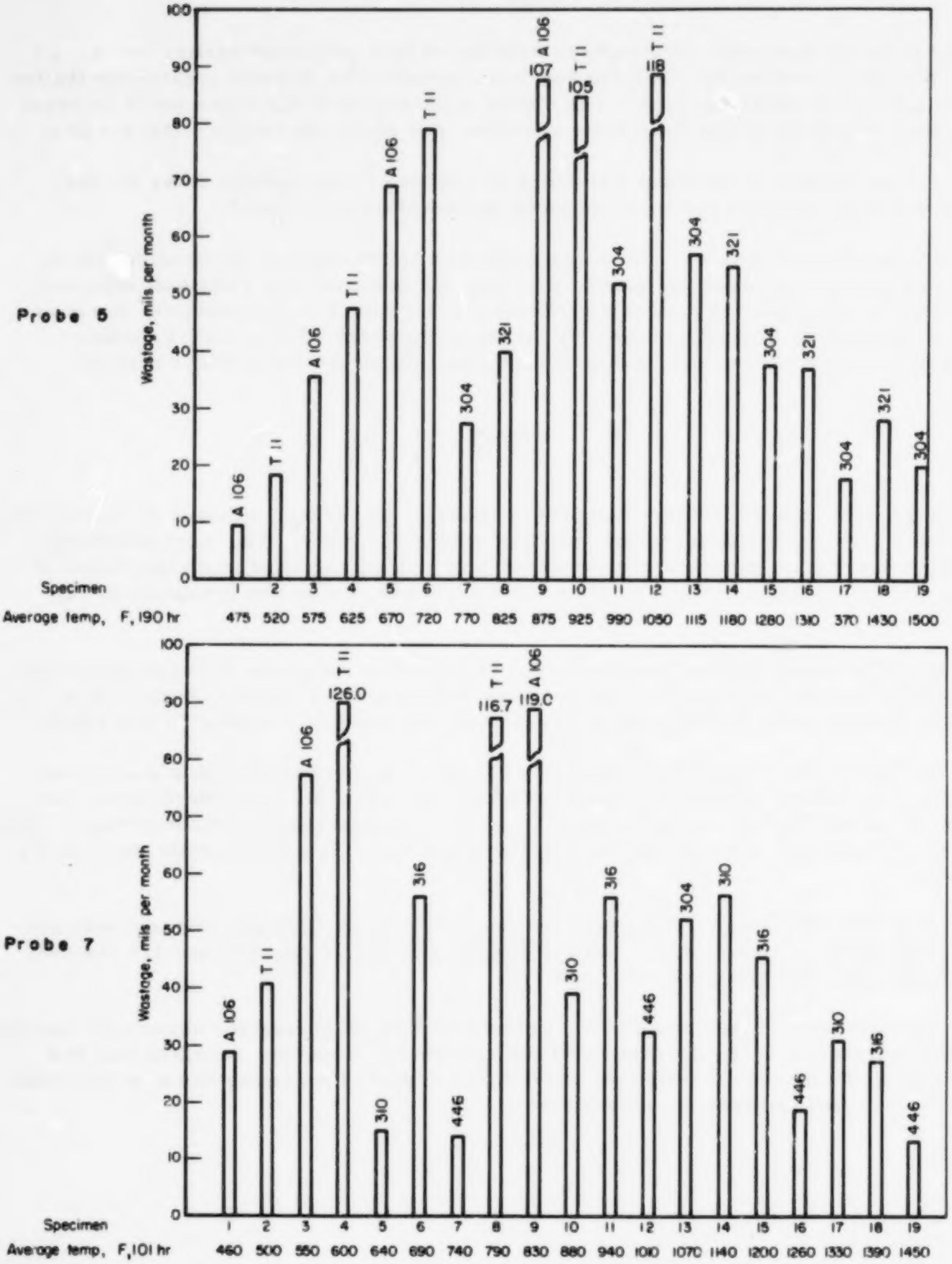


FIGURE 11. TUBE WASTAGE RATES FROM EXPOSURE IN FLAME AREA

Table A-1 in the Appendix. Comparison with the results presented earlier for Area 1 shows that the corrosion for identical specimen temperature is much greater for the two probes exposed in the flame area. The higher temperature of the flame would increase the deposit temperature and accelerate reactions just above the cooler metal surface.

As can be seen in the upper bar graph in Figure 11, the wastage rates for the carbon steels increased rapidly as the metal temperatures increased.

The stainless steels were severely attacked at temperatures above about 900 F. As can be seen in the lower bar graph, the Type 446 material was somewhat superior to the others examined. It may be significant that the attack on the stainless steels appears to go through a maximum over the temperature range 1000 to 1200 F, which corresponds to the range where enhanced sensitization of austenitic alloys occurs.

Norfolk

In general, the three corrosion probes (Runs 8, 10, and 11) exposed at Norfolk suffered much less corrosion than those exposed at Miami County. The most noticeable exception was the low-temperature end of Probe 8, which corroded much like those of Miami County. Details of wastage rates for the Norfolk probes are presented in Figure 12.

It will be noted that the Norfolk probes did not show the marked rise in corrosion rate with an increase in specimen temperature as was found at Miami County. It is believed that the lower ambient gas temperatures at Norfolk are related to this effect.

Norfolk Probe 11 was in the furnace 2304 hours and during this time was at temperature 1318 hours. A comparison of corrosion rates for this run with the other two at Norfolk shows that the corrosion rate decreased as the exposure time increased. This decrease is believed to be associated with the protective action of the scale found on the pipe wall.

Very little difference can be seen between results for A106 as compared with the T11 carbon steel on these probes. Of the stainless steels, Types 446 and 310 seemed slightly superior to Types 304, 321, and 316.

The corrosion results for Probe 11 show that both aluminum and chromium coatings furnished protection. The appearance of the specimens, however, indicated that this protection would be only of relatively short duration since the coating had been corroded away on about half the area on many pieces.

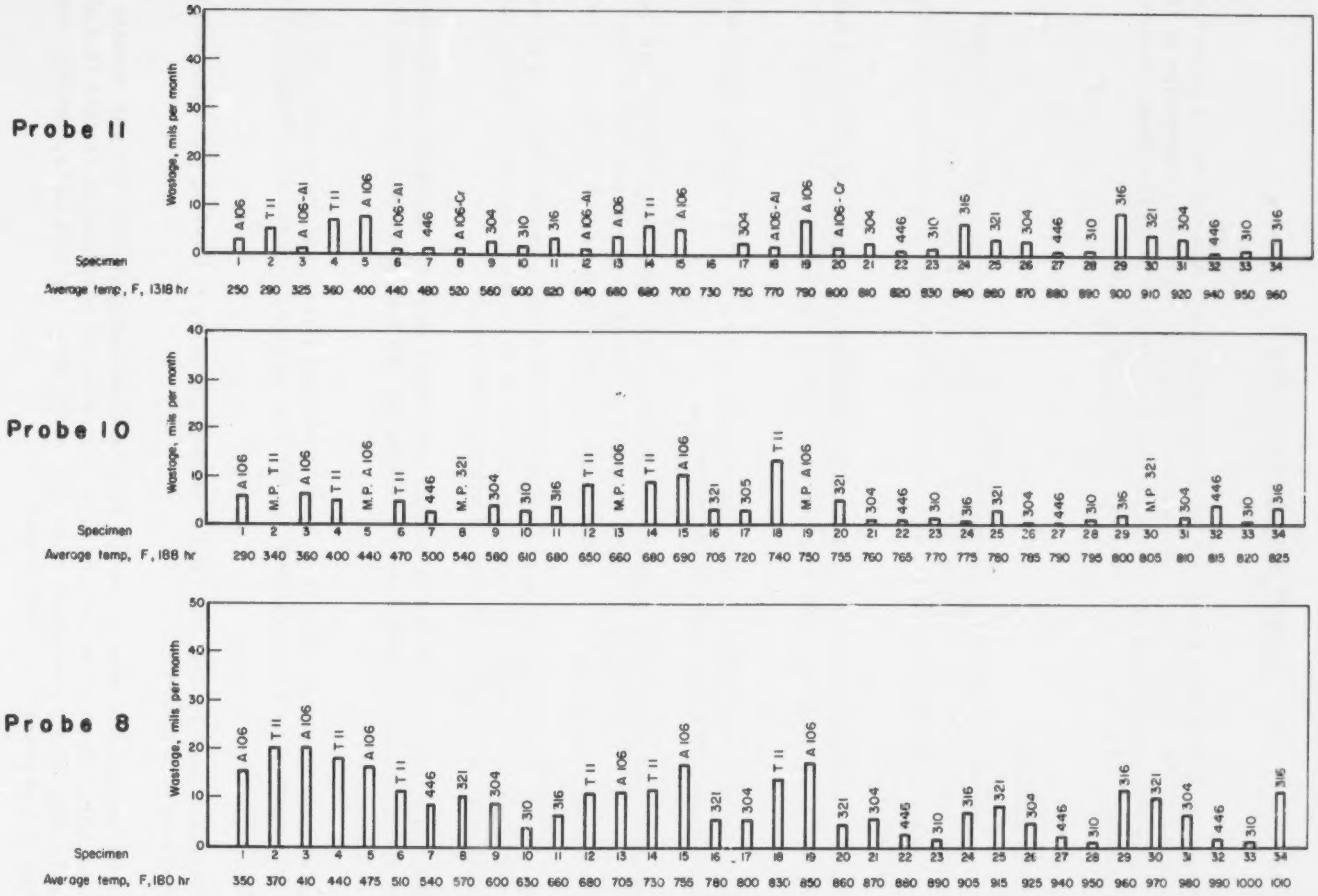


FIGURE 12. TUBE WASTAGE RATES ON PROBE EXPOSED AT NORFOLK

CHEMICAL SPECIES RESPONSIBLE FOR CORROSION

Furnace-Gas Compositions

Understanding of the mechanism by which deposits form and corrosion occurs on the metal surfaces of the incinerator, among other things, requires a knowledge of the furnace-gas composition. Sampling of these gases has been done at the Miami County, Ohio, the Oceanside, New York, and the Norfolk, Virginia, sites.

Methods of Measurement

Ordinary combustion-gas measurements to determine carbon dioxide, oxygen, and carbon monoxide were made by standard Orsat methods, Fyrite analyzers, and the Bailey Heat Prover. The water content was measured by condensing the moisture and determining its volume.

Sulfur oxides were sampled by bubbling flue gas through 1 percent hydrogen peroxide solution and analyzing the resulting sulfuric acid by the barium chloranilate method.

Chloride analysis was made on this same solution by decomposing the H_2O_2 with MnO_2 and titrating the chloride with silver nitrate.

Fluoride analysis was made with an ion electrode (Orion). Gaseous HF was converted to SiF_4 by reaction with glass and absorbed in a buffered test solution. The chloride content was verified by using a chloride-ion electrode on this same solution.

Total acidity in the flue gases also was monitored using a modified SO_2 analyzer (Instrument Development Company), which is based on the measurement of the electrical conductivity of an absorbing solution of hydrogen peroxide.

Nitrogen oxides were sampled in 3-liter evacuated flasks. Analyses were made by the phenol disulfonic acid method recommended by the Los Angeles County Air Pollution Control District.

Aldehydes also were sampled in 3-liter evacuated flasks and were analyzed by the sodium bisulfite method as recommended by the Los Angeles County Air Pollution Control District.

A check was made for unburned hydrocarbon gases by collecting a 3-liter sample for mass-spectrometer analysis.

In one run an analysis was made for SO_3 by condensing it from the gas stream and determining sulfate. Normal boiler practice in coal-fired installation results in a flue gas in which the SO_3 levels are about 1 percent of the SO_2. In this case, the SO_3 concentration was 0.3 percent of the SO_2 found.

Results and Discussion

As would be expected from the variable nature of the solid waste burned in municipal incinerators, a wide range of values for the different gases was found. The data are summarized in Table 3.

TABLE 3. FURNACE-GAS COMPOSITIONS

	Concentration Ranges		
	Miami County	Oceanside	Norfolk
SO_2, ppm	2-303	0-100	0-10
HCl, ppm	5-115	1-330	14-75
HF, ppm	Traces-0.6	Traces-1.1	Traces-6.0
Nitrogen Oxides, ppm	10-138	107(a)	4-7
Organic Acids, ppm	35-136	Not measured	150-340
Oxygen, vol %	15.0-9.5	17.0-8.0	16.5-15.0
CO_2, vol %	6.0-10.8	3.5-12	3.9-5.6
CO, vol %	Traces-0.2	0.005(a)	0.1-0.2

(a) Single measurement.

Two gases of primary concern from the corrosion standpoint are SO_2 and HCl. The amounts of these gases found in each of the three incinerators varied greatly. The maximum values are not much over 100 ppm, except for one measurement for HCl of 330 ppm at the Oceanside incinerator and 300 ppm SO_2 at Miami County. In general, the SO_2 and HCl concentrations at Norfolk were less than those at the other sites. This could have some relationship to the lower corrosion experienced at Norfolk, although factors such as temperature are probably of even greater importance.

It can be noted in Table 3 that the SO_2 concentrations are relatively low compared with those for large coal- and oil-fired boilers, which usually range from 2500 to 3000 ppm. On the other hand, such boilers do not contain the HCl found in incinerators. Even at low SO_2 levels, as the next section of this report shows, accumulation of sulfates in the incinerator deposits reach the same levels (20 to 30 weight percent) in a few hundred hours as are commonly found in power-station boilers after thousands of hours of service. Although the HCl levels in the incinerator gases are generally of the same magnitude as the SO_2 levels, the amounts of chlorides found in the deposits are smaller than the amounts of sulfates, presumably because of the conversion of chlorides to sulfates and loss of the chlorine.

SO_3 was not believed to be a significant factor. One such measurement at Miami County showed 1 ppm SO_3 and 303 ppm SO_2 in the flue gases at the position where the probe was exposed.

It is concluded that SO_2 and HCl were present in sufficient concentrations in all three incinerators to be of concern from the standpoint of possibilities of corrosive conditions.

The amount of HF found at Norfolk (6 ppm) is appreciably greater than the amounts detected at the other two sites. No indications have been found that this gas is of great significance in the tube-metal-wastage process.

Concentrations of nitrogen oxides were in general lower (4 to 7 ppm) at Norfolk than at the other sites, where they ranged up to 100 ppm. On the other hand, greater amounts of organic acids (up to 340 ppm) were measured at Norfolk than at Miami County (136 ppm). The high values for organic acids most likely stem from the large amounts of wood burned at Norfolk. While the nitrogen oxides and organic acids contribute to the acidity of the furnace gases, they probably play larger roles in scrubber corrosion, where they are absorbed in wash water, than in fireside corrosion. Laboratory experiments made during this study have shown that formic acid vapors have negligible corrosion effects on the steels used.

The combustion gases in the three incinerators contained typical levels of the normal combustion gases CO_2, O_2, and CO. Less excess air is used at Norfolk, as temperature reduction is provided more effectively by the water walls and the boiler convection surfaces.

Gas velocities were measured at two areas in the Miami County incinerator. The flow was about 2100 fpm at Location 1 and about 450 fpm near Location 2.

Relation of Solid Waste to Gas Composition

In order to relate the nature of the solid waste burned to the composition of the furnace gases, observations were made during six consecutive operating days at the Miami County incinerator in April, 1970. A checklist of typical classes of materials in the solid waste was drawn up, and the presence of a relatively large amount (5 percent or more) of any item was noted. At the same time, the gases in the incinerator were analyzed for SO_2, HCl, HF, nitrogen oxides, organic acids, and particulates. A summary of the data, with duplicate analyses in some cases, is presented in Figure 13. The upper half of the figure shows the concentrations of the gaseous components of the furnace gases, while the lower half shows the amounts of various materials in the hopper feed to the incinerator during the sampling period. Any materials present in amounts of 5 percent or more are included in the figure. Lesser amounts of material could not be estimated, so the totals for each day are slightly less than 100 percent.

Although it is difficult to draw any firm conclusions from the nature of the solid waste and the furnace gases, some observations can be made:

(1) Organic acids were the predominant component on four of the days; on these days, corrugated boxes, paper products, or wood were present in large amounts.

(2) The amount of HCl found was significantly below the 100 ppm level which was observed on several other occasions. The presence of 5 to 10 percent of plastics in the waste did not cause any large increase in HCl concentration. The type of plastic being burned was not identifiable, however.

(3) The very small amount of HF detected on these days agrees with that found on other occasions, and probably is typical.

(4) The large amount of nitrogen oxides observed on the last day may be related to the fact that this was the only day on which garbage was present in a notable amount.

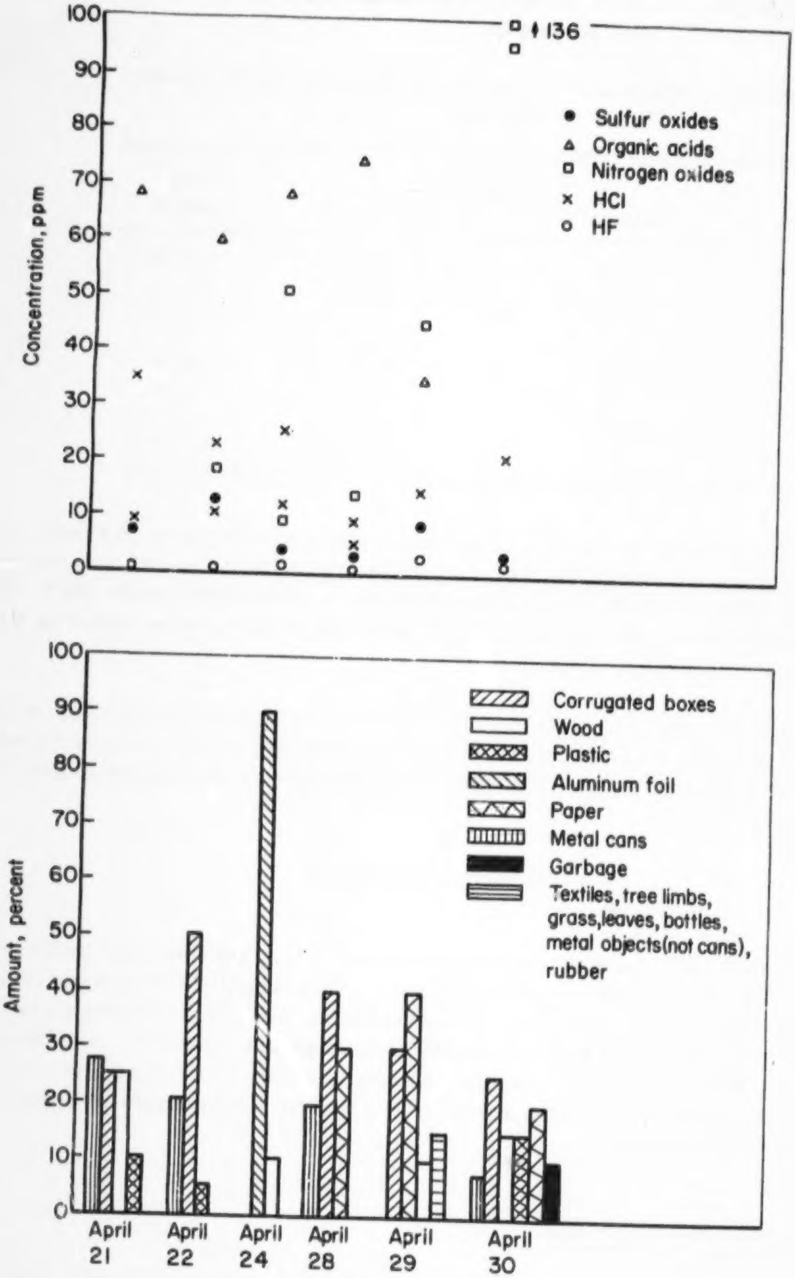


FIGURE 13. COMPARISON OF FURNACE-GAS COMPOSITION AND SOLID WASTE AT MIAMI COUNTY INCINERATOR

Materials in quantities of less than 5 percent are not included on the bar graphs, so the totals for each day are slightly less than 100 percent.

The amounts of particulates found in the furnace gases are shown in Table 4. They range from 0.36 to 2.40 lb/1000 lb of gas.

TABLE 4. PARTICULATE CONTENT OF FURNACE GAS AT MIAMI COUNTY INCINERATOR

Date	Particulate Loading		CO_2, percent
	Grains/SCF	Lb/1000 Lb Gas	
April 21	0.25	0.48	3 to 4
	0.23	0.44	--
April 22	0.35	0.66	3 to 7
April 24	1.27	2.40	--
April 28	0.23	0.44	3 to 15
April 29	0.27	0.51	2 to 4
	0.49	0.93	4
April 30	0.19	0.36	4 to 6

On April 24 a fairly large quantity of particulate matter was present, i.e., 2.40 lb/1000 lb gas; on that day, the chief item being burned was aluminum foil from an industrial source. This resulted in large amounts of aluminum oxide dust. In fact, on some occasions small particles of unoxidized aluminum have been found in the probe deposits at the Miami County incinerator.

It appears that in order to obtain a reliable correlation between the solid waste being burned and the nature of the furnace gases, it would be necessary to add known amounts of various materials and determine the changes in the furnace-gas components.

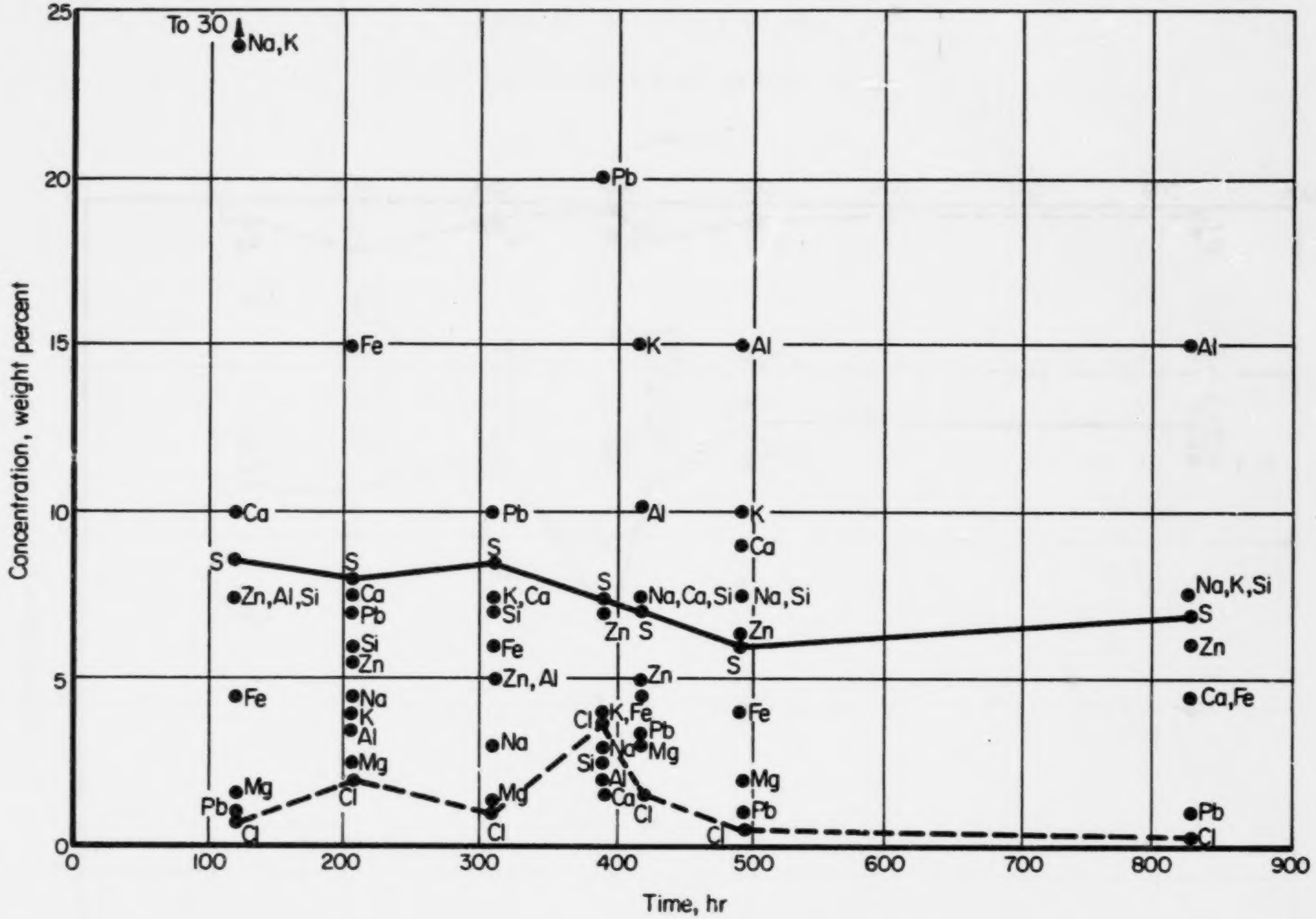
Analysis of Deposits

In order to establish the causes and mechanisms of incinerator boiler-tube corrosion, analysis of the tube deposits is important. This analysis provides information regarding the distribution of corrosive components in different temperature zones and also provides identification of specific compounds that are present. Emission spectrography and wet-chemical techniques have been used to determine the concentration levels of the various elements in the deposits. Specific compounds present have been identified by X-ray diffraction.

Miami County Incinerator Deposits

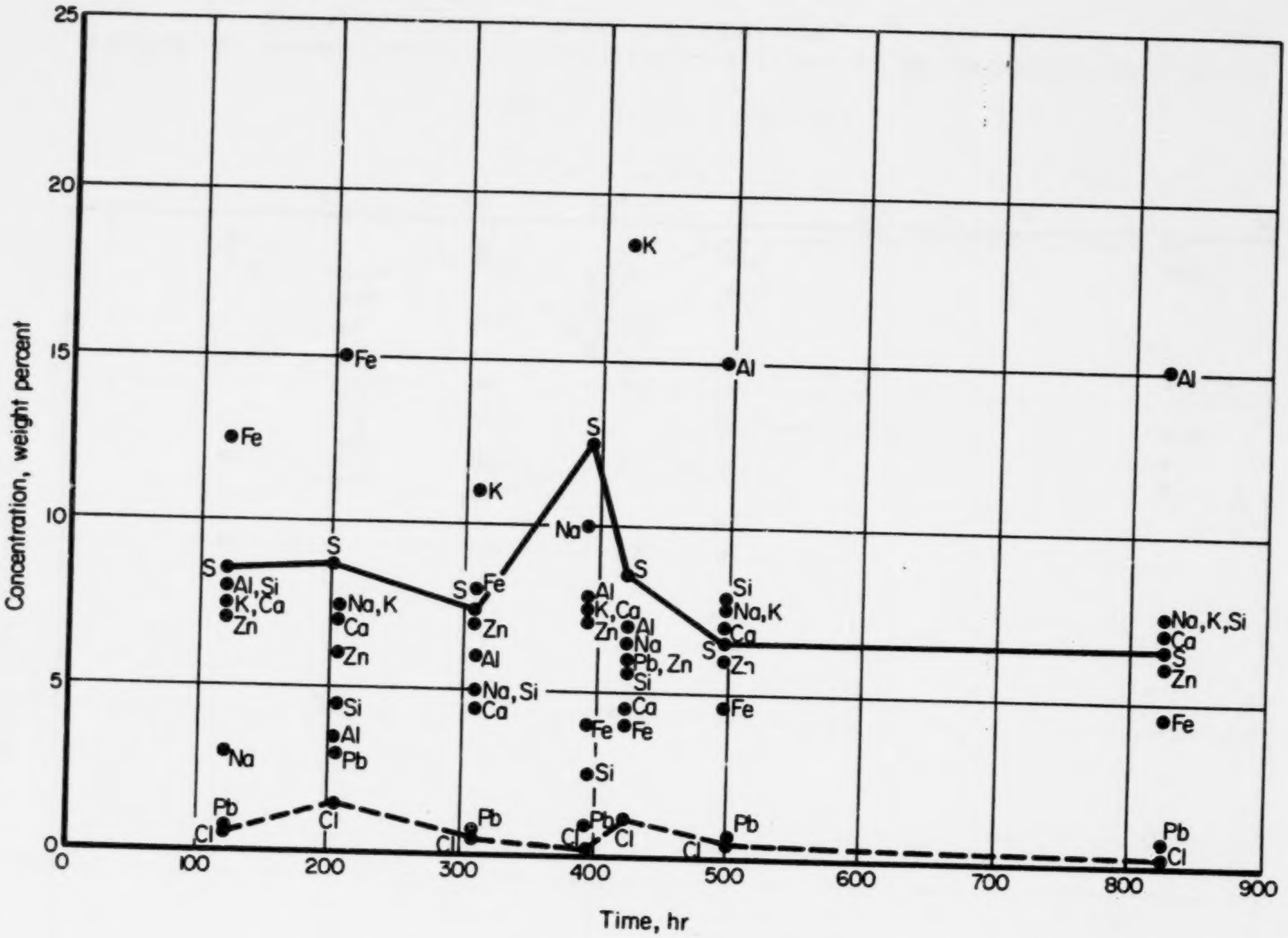
Deposits from the corrosion probes exposed at the Miami County, Ohio, incinerator have given insight into the deposition process and the chemical reactions involved.

The distributions of chemical elements found in significant quantities on the corrosion probe as a function of time are shown in Figure 14. These exposures cover periods of about 100 to 828 hours and constitute analyses of deposits from seven probe exposures, all made over the bridgewall of the incinerator. Four temperature zones along the length of the probe have been selected for consideration. The changes in sulfur and chlorine concentration have been emphasized by connecting the points in the



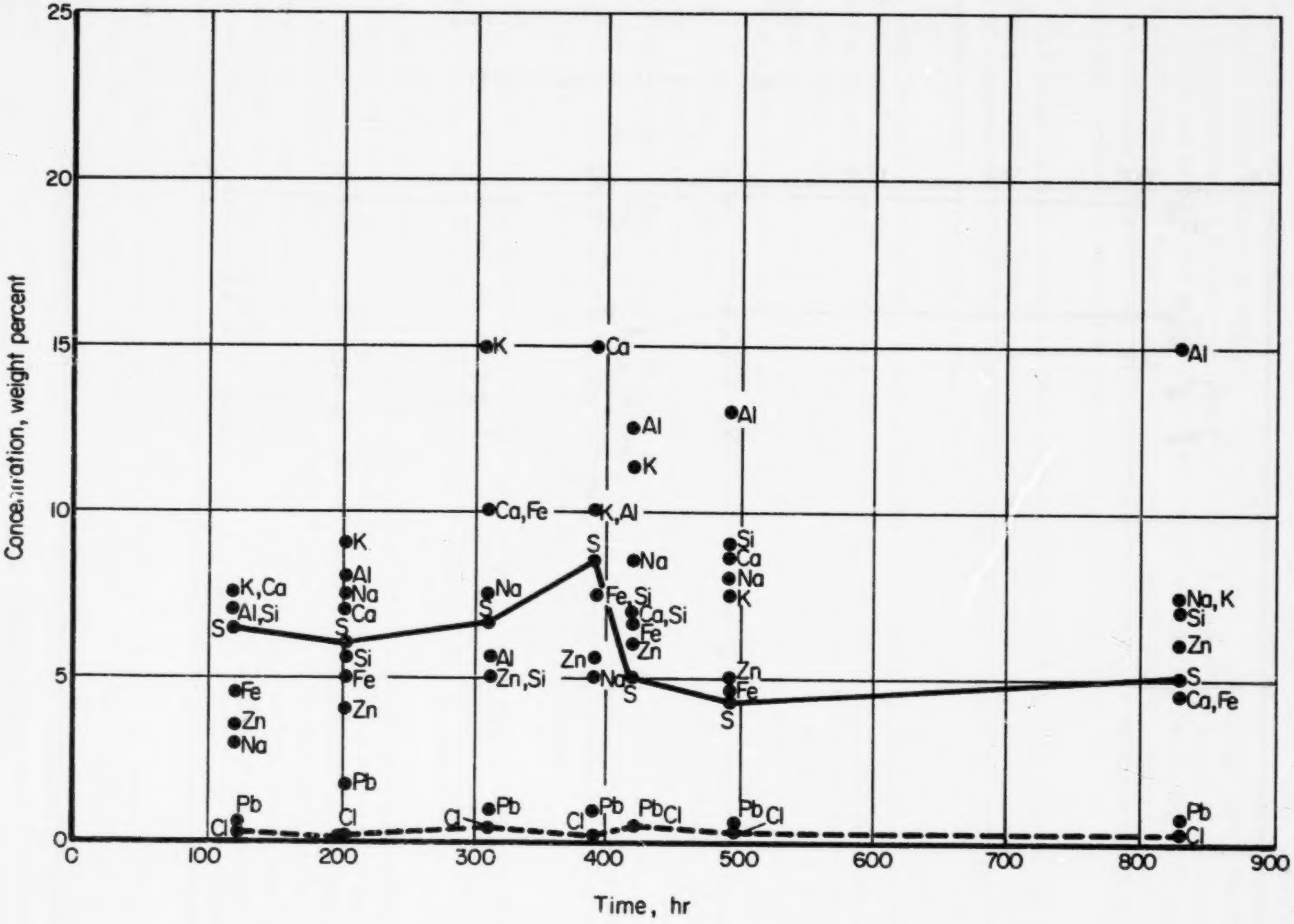
a. Temperature Zone of 250-500 F

FIGURE 14. PROBE DEPOSIT COMPOSITION AS A FUNCTION OF EXPOSURE TIME IN THE MIAMI COUNTY, OHIO, INCINERATOR



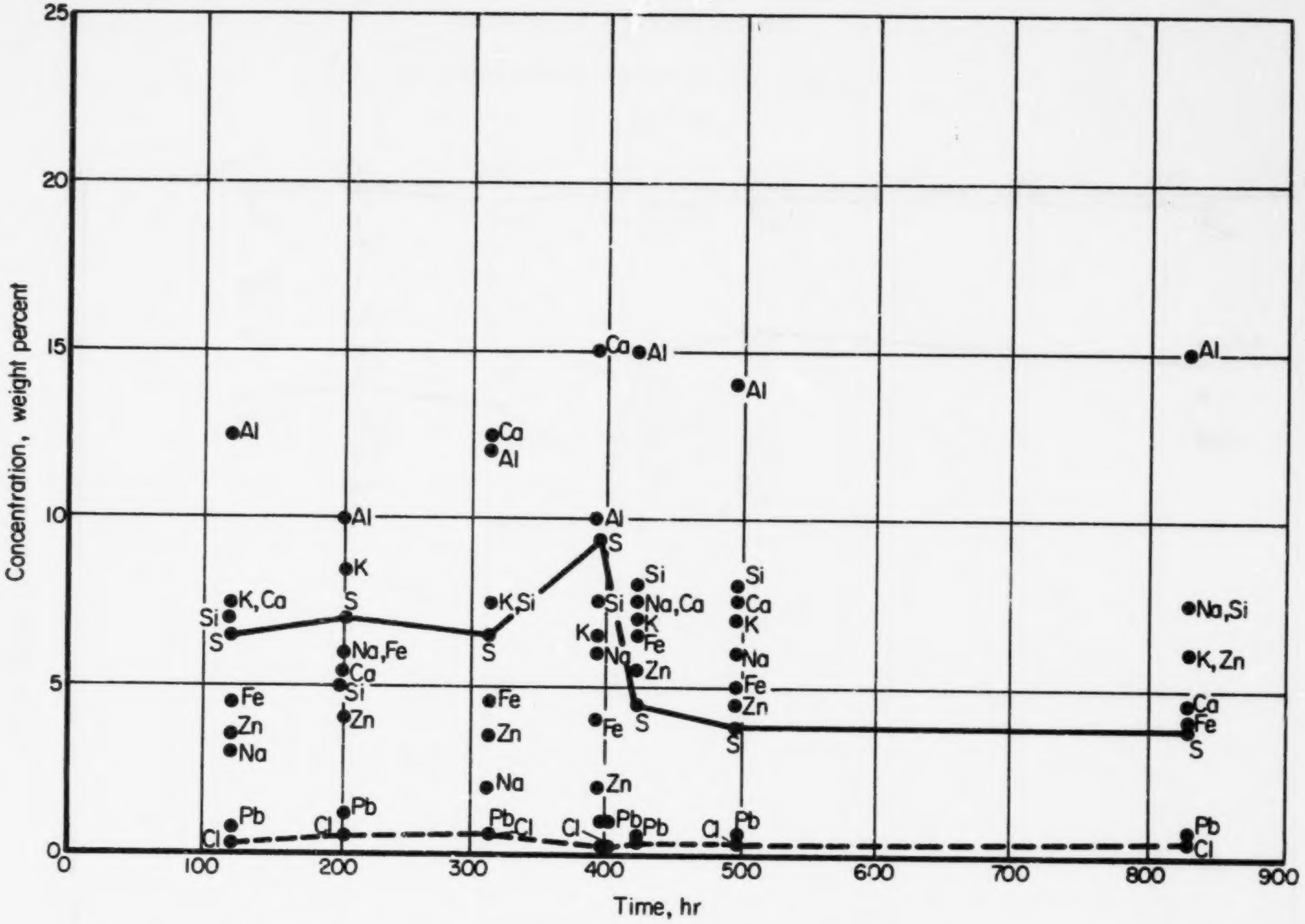
b. Temperature Zone of 500-750 F

FIGURE 14. (CONTINUED)



c. Temperature Zone of 750-1000 F

FIGURE 14. (CONTINUED)



d. Temperature Zone of 1000-1250 F

FIGURE 14. (CONTINUED)

figure, as these elements are of great significance in the corrosion process. The sulfur concentration goes through a maximum at about 400 hours in three temperature zones, and the chloride does the same in the lowest temperature zone. However, these peaks represent data obtained from a single probe and may reflect some unusual nature of the waste being burned during the period in question. Additional data would be required to establish the sulfur maximum as a fact. Nevertheless, it is important from the aspect of corrosion that the sulfur level builds up rapidly in the deposits and after 100 hours is almost as high as it ever becomes. At the higher temperatures the sulfur level is somewhat reduced, probably because of the volatility of some of its compounds, but it is still present in sufficient quantity to cause corrosion.

The same is true of the chlorine content of the deposits. At low temperatures the chlorine persists in the deposits because of lowered volatility of chlorides and slower rates of conversion to sulfates. However, even the small quantities present in the high-temperature zones can cause serious corrosion.

High percentages of sodium and potassium were found in the low-temperature zone of the shortest probe run, with decreasing amounts in the longer exposure periods. Some differences may be attributed to the variations in the waste being burned at any given time, but these results also indicate that the sodium and potassium compounds deposited initially have been converted to other forms during longer exposure times. It is likely that the sodium and potassium deposited initially as oxides or possibly chlorides were converted to sulfate by reaction with SO_2 and oxygen during the exposure period. Sulfates are the dominant form of alkalies in tube deposits in coal-fired boiler furnaces. This conversion to compounds of higher molecular weight results in lower percentages of sodium and potassium in the deposits. X-ray-diffraction data have shown that NaCl, KCl, Na_2SO_4, and $(Na, K)SO_4$ all exist in the deposits, but the amount of chloride is always less than that of sulfate even though there is as much HCl as SO_2 in the furnace gases; this indicates conversion of chloride to sulfate.

The conversion of sodium and potassium oxides to chlorides by HCl in the furnace gases and ultimately to sulfates by reaction with SO_2 would result in the deposition of potentially corrosive chloride-sulfate mixtures on the metal surfaces.

Both the lead and the chloride concentrations were highest in the low-temperature zone of these probes. This result may reflect higher volatility of the compounds containing these elements at high temperatures, as well as more rapid conversion of oxides and chlorides to sulfates under such conditions. The fact that PbO, $4PbO \cdot PbSO_4$, and $PbSO_4$ have been identified in the deposits by X-ray diffraction shows that there is stepwise conversion of the lead oxide to lead sulfate via the intermediate oxysulfates. The unusually large amount of lead found in the 400-hour deposit probably resulted from the burning of some waste with a high lead content during the exposure period.

As the exposure time was lengthened, aluminum became the predominant element in the deposits, and the amounts of sodium, potassium, calcium, and silicon were significant. This indicates that clay-like materials such as silicates containing sodium, potassium, calcium, and aluminum were formed on long-term exposure. Materials of this type, forming a hard deposit, can build up above the metal surface a protective layer that is chemically inactive and serves as a barrier to diffusion of sulfur oxides, oxygen, and HCl. The decrease in the corrosion rates with time are indicative of such protective action.

The long-term exposure of Probe 9 (828 hours) resulted in a buildup of deposits up to 3 inches in depth along the probe. Visual examination of the deposits indicated that there were differences between the bulk of the deposit and the scale that formed near the specimen surfaces. Consequently, this deposit was separated into layers: (1) the scale next to the metal and (2) the bulk deposit used for analysis. The differences observed are shown in Figure 15. There was a greater concentration of potassium, lead, zinc, iron, chlorine, and sulfur in the scale than in the deposit at all temperatures. On the other hand, aluminum and silicon were present in significantly greater amounts in the bulk of the deposit at all temperatures. It will be noted that the amount of lead and chlorine in both deposit and scale decreased as the temperature increased. These data are in agreement with the results of the electron-microprobe examination of the probes, which revealed that potassium, lead, sulfur, and chlorine were present at the metal-deposit interface on corroded specimens.

The analyses of deposits on Probes 5 and 7, which were in a region of high gas temperature near the flame zone of the incinerator, are shown in Figure 16. The most notable features in these deposits are the high iron and silicon contents and the low sulfur. Iron and silicon were present in substantially greater amounts than in corresponding temperature zones of the probes which were not directly exposed to the flames, while the sulfur was quite low. The analysis indicates a more highly oxidized condition in these deposits than in those collected further from the flame. Although the metal-specimen temperatures for three of the zones were the same as those in other probes, the deposit was subjected to higher gas temperatures which could have volatilized some of the compounds formed in the deposits.

A relatively short experiment was run at the Miami County incinerator in which a water-cooled probe was withdrawn at intervals of 2, 8, 24, and 88 hours for removal of deposits. The results of the deposit analyses are shown in Figure 17. However, no analyses were made for sulfur in these deposits. Extremely high concentrations of chlorine and of iron were found in these deposits, indicating that chloride corrosion begins early in the exposure. As the chlorides are converted to sulfates and pyrosulfates later in the exposure, corrosion by these compounds adds to the mutual wastage. In the early stages of the deposit history, the lead concentration also is high, probably as PbO, and the relative amount of lead decreases as this compound is converted to $PbSO_4$. The potassium and zinc concentrations remained fairly constant during the time in which these deposits accumulated, while the aluminum and silicon increased slightly.

Norfolk Incinerator Deposits

Three probe exposures were carried out at the Norfolk incinerator. The distribution of elements in the deposits as a function of temperature is shown in Figure 18. It is significant that lead and sulfur predominated in the deposits. The average chlorine content was higher than that found in the long-term exposures at the Miami County incinerator. These facts show that there was more than enough potentially corrosive material present in the Norfolk incinerator deposits to cause metal wastage, if other conditions were favorable. The factors that minimize corrosion at Norfolk appear to be the relatively low metal temperatures and the small temperature gradient through the deposit.

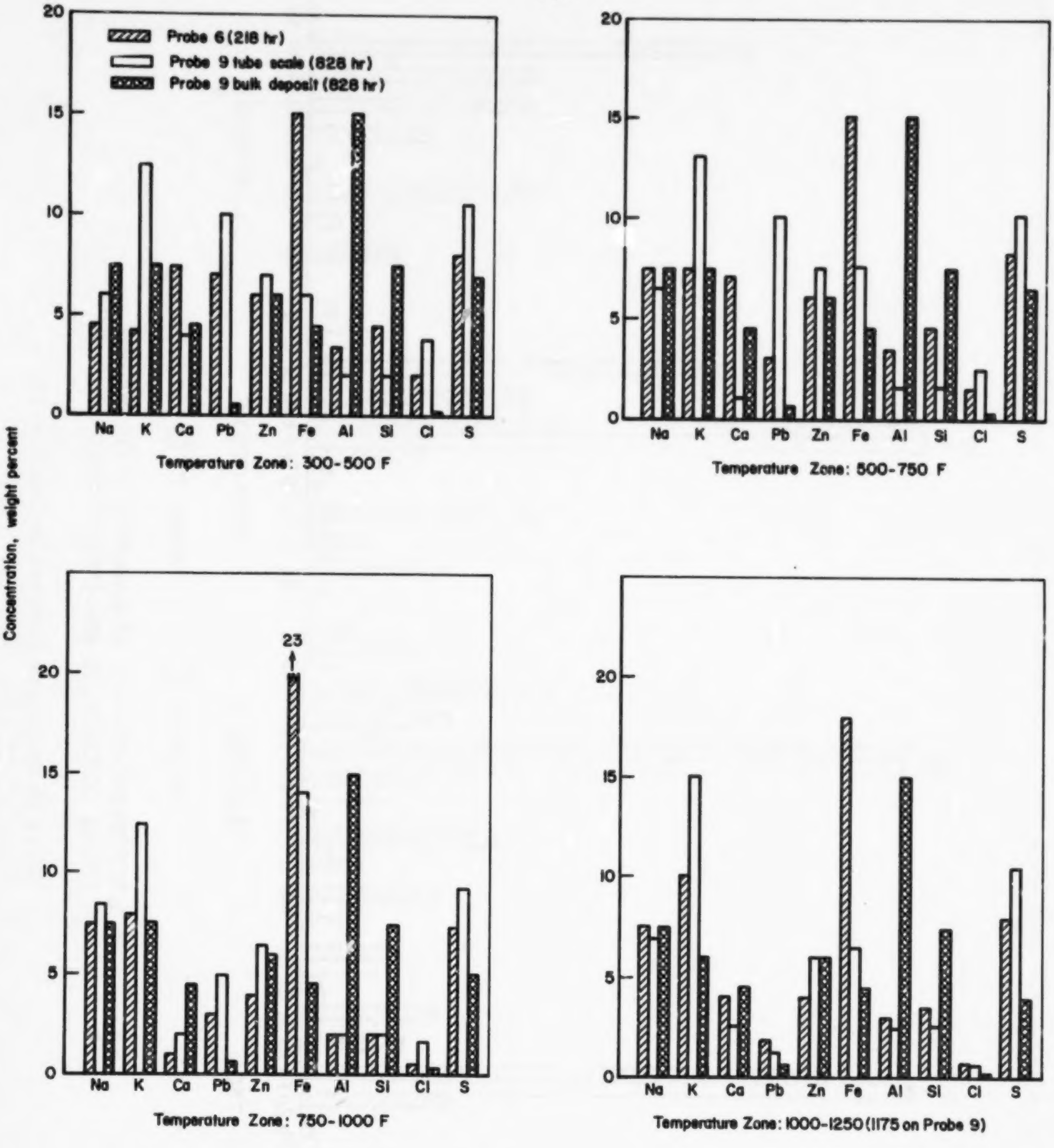


FIGURE 15. DISTRIBUTION OF ELEMENTS IN DEPOSITS FROM CORROSION PROBES 6 AND 9

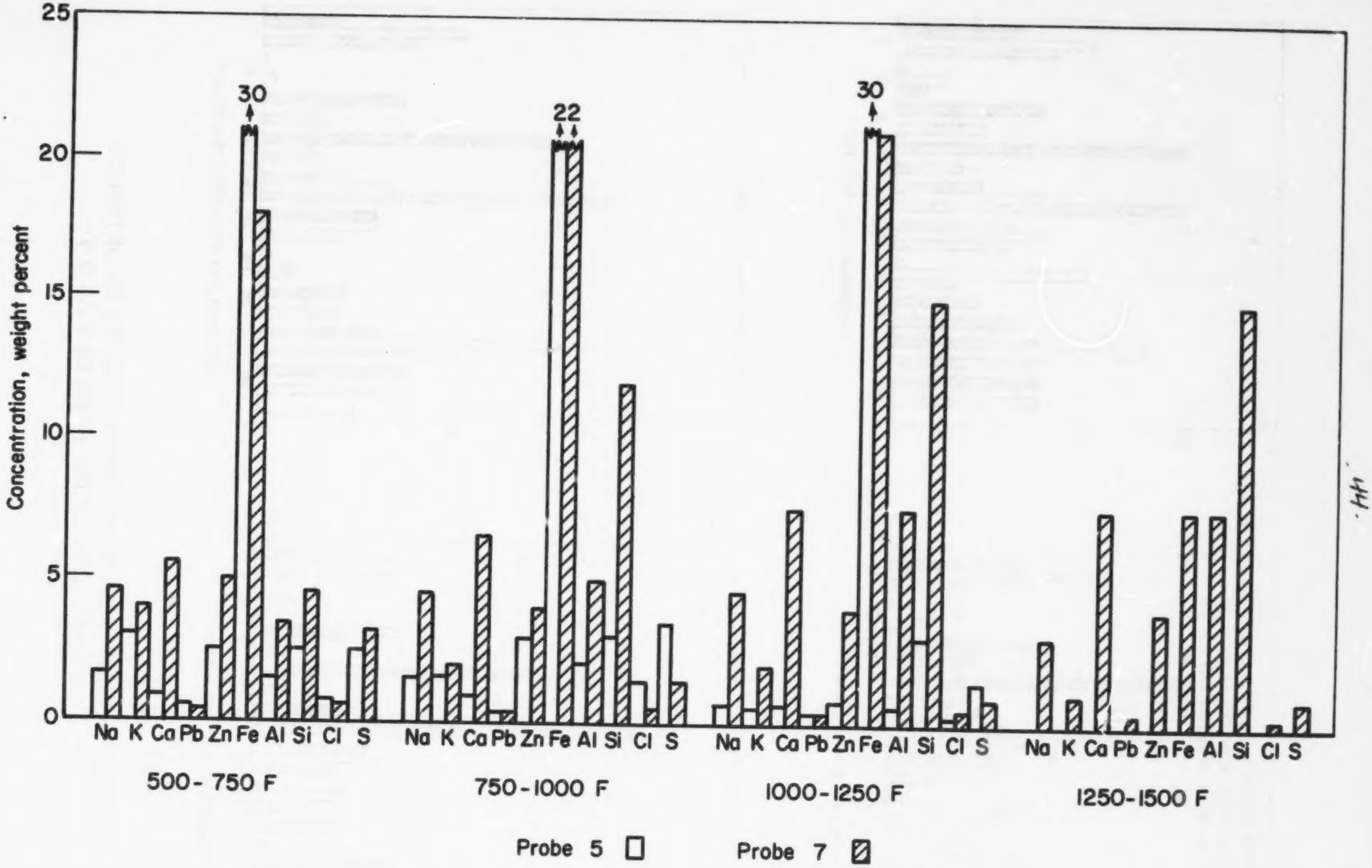


FIGURE 16. DISTRIBUTION OF ELEMENTS IN DEPOSITS FROM CORROSION PROBES 5 AND 7

These probes were exposed in flame area.

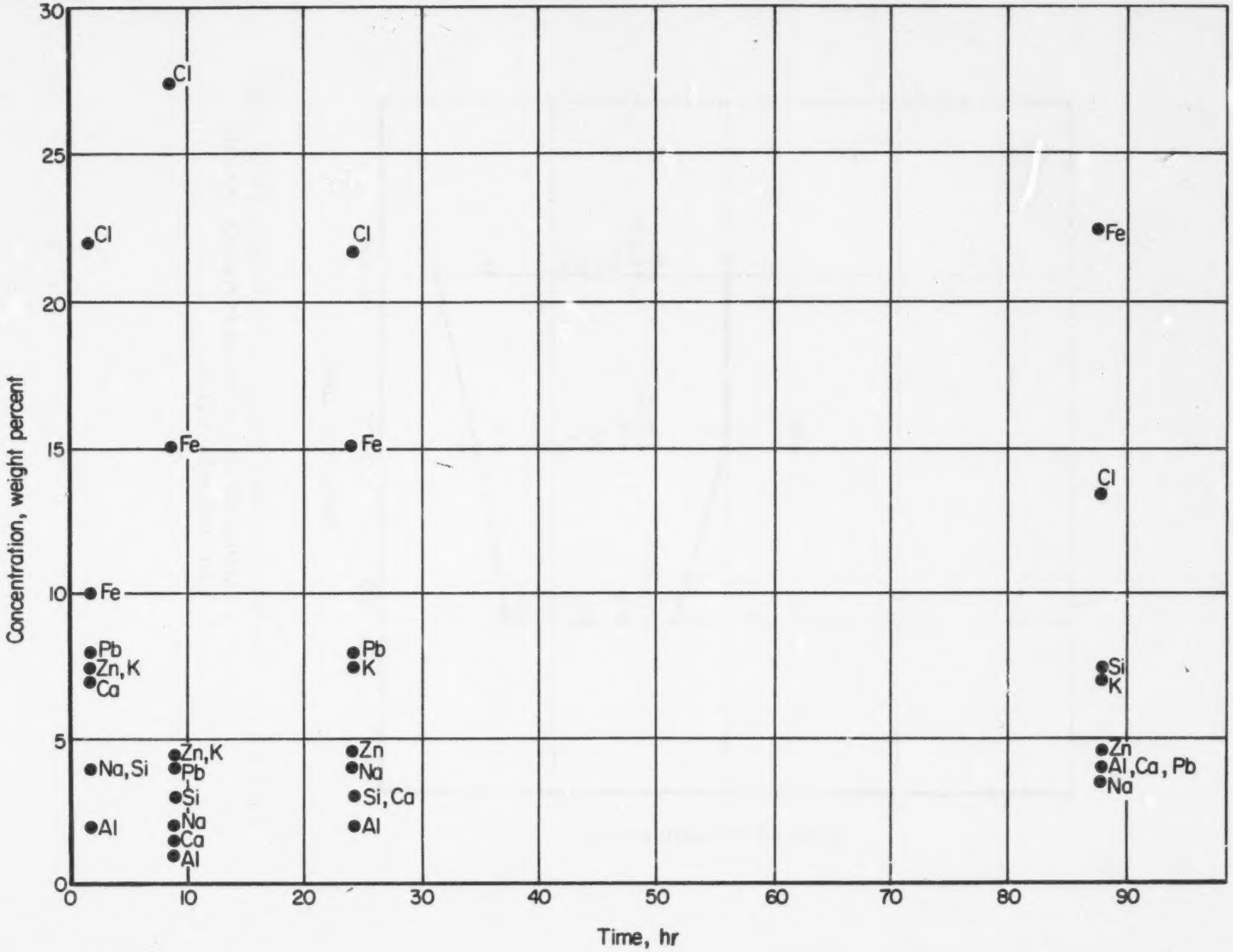


FIGURE 17. COMPOSITION OF PROBE DEPOSITS FROM SHORT-TERM EXPOSURE IN THE MIAMI COUNTY INCINERATOR

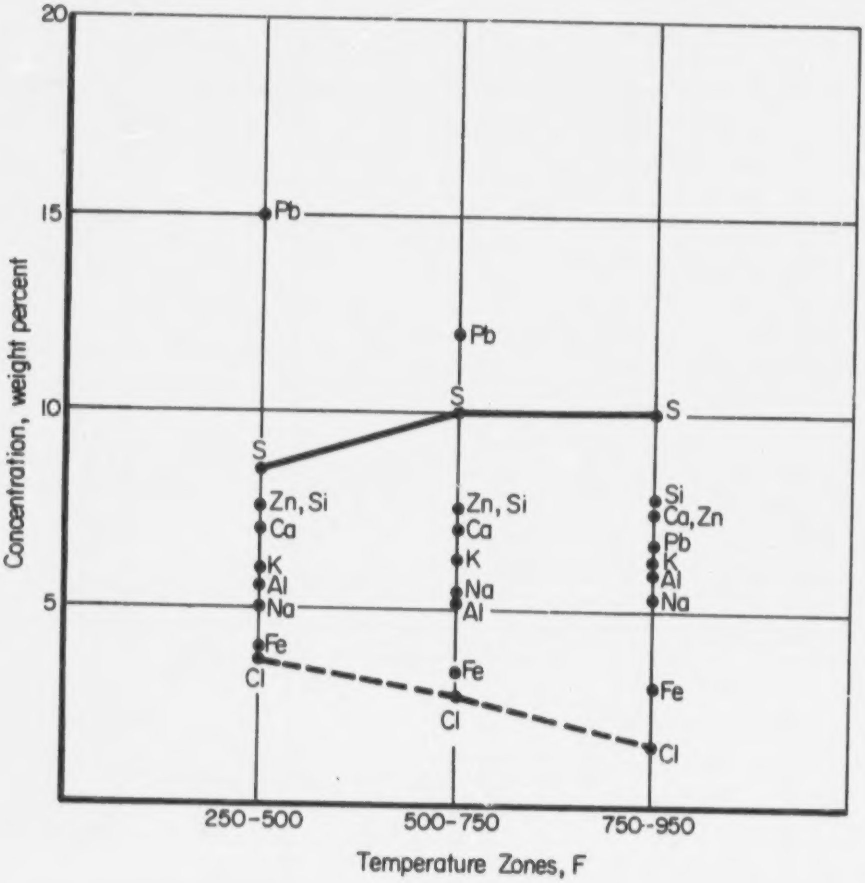


FIGURE 18. PROBE-DEPOSIT COMPOSITION AS A FUNCTION OF TEMPERATURE FOR EXPOSURES IN THE NORFOLK INCINERATOR

Some specific points of difference between the Norfolk deposits and the Miami County deposits were noted:

(1) The lead concentration was significantly higher on Probe 10 at Norfolk, particularly at temperatures above 500 F. However, this high lead concentration did not result in greater corrosion.

(2) Sulfur was the predominant element in all temperature zones, although it was not present in unusually large amounts. No such predominance of one element has been noted in the Miami County deposits.

(3) In general, deposits on the probes at Norfolk have been less voluminous and more powdery than those at Miami County.

(4) A significant observation concerning Probe 10 at Norfolk was that less sulfide was present on the specimens, as compared with probes at Miami County or Probe 8 at Norfolk. In addition, fewer acidic areas as revealed by moistened pH indicator paper were present on the mildly corroded specimens from Norfolk as compared with those from Miami County. This means that less reaction with sulfur-containing salts had occurred and that fewer compounds such as pyrosulfates were present.

Sulfide and pH Tests

All specimens except those used for special electron-microprobe or X-ray studies were subjected to testing by sodium azide solutions for the presence of sulfide, and to moist pH indicator paper for acidity or alkalinity. These tests were made on specimens with the bulk deposit removed mechanically.

A summary of the results obtained on nine probes is provided in Table 5. The presence of sulfide is indicated by a + sign. A double ++ denotes a very strong reaction, i.e., evolution of many N_2 gas bubbles. The pH values were estimated from the color obtained on Universal pH paper, and show gross effects only.

Considering first the results for the presence of sulfide:

(1) Sulfide was found on the majority of specimens.

(2) At Miami County, the lowest concentrations of sulfide were found predominantly on the high-temperature specimens of Probes 2 and 6 and scattered over the length of Probes 5 and 7. This is consistent with the fact that Probes 5 and 7 were operated at higher temperature.

(3) At Norfolk, very little sulfide was found on the low temperature specimen on Probe 10; several pieces at higher temperatures also gave a negative reaction.

It should be mentioned that in some instances it was necessary to scratch through the oxide scale and expose base metal before the sulfide test was positive. This is taken to mean that the sulfide was formed very near or in the metal surface.

TABLE 5. RESULTS OF SULFIDE AND pH TESTS

Specimen Number	Probe 2		Probe 3		Probe 4		Probe 5		Probe 6		Probe 7		Probe 8		Probe 9		Probe 10	
	Sulfide	pH	Sulfide	pH	Sulfide	pH	Sulfide	pH	Sulfide	pH	Sulfide	pH	Sulfide	pH	Sulfide	pH	Sulfide	pH
1	+	3			+	3	neg	4-8	+	3-8	+	3	+	9			neg	3-8
2	+	3	+	2	+	2	neg	4-8	++	3-8	neg	9	++	3	++	3	neg	3-8
3	+	4	+	2	++	2	trace	9	++	3	+	4	++	3-8	++	3-8	neg	3-8
4	trace	4	++	7	+	3	+	4	+	2	+	7	+	4-8	+	3	++	3-8
5	++	4			++	3	+	4-8	+	2	+	9	+	4-8	++	3	+	3-8
6	+	2			++	3	++	10	+	3	+	3	++	4-8	++	3	+	4-8
7	++	2	++	2	+	3	neg	10	+	3	neg	3	+	4-8	neg	3	++	9
8	+		++	3	++	4	trace	10	+	2	++	3	++	4-8	++	3	++	4-9
9	+		++	2	+	4	+	4-8	++	3	++	7	+	4-8	+	3	+	4-9
10	+	2			+	3	++	4-8	+	4	++	10	++	3-8			++	9
11	+		++	3	++	3	neg	4-8	+	3	+	7	++	3-8	++	3	++	4-9
12	+		+	2	++	4	+	4-8	+	3	+	9	++	3-8	++	3	++	4-9
13	++	2	++	3	++	4	trace	4-8	++	3	+	8	++	3-8	++	3	+	4-8
14	++	7	+	3	++	3	neg	4	+	4	+	7	++	4-8	++	3	++	4-9
15	++	3			++	7	neg	4-8	+	7	+	7	++	4-8	++	3	++	5-9
16	+		+	3	++	7	+	4-8	+	7	neg	8	+	4-8	++	3	++	5-9
17	+		+	4	+	7	+	4-8	+	7	+	7	+	3-5	++	3	+	4-9
18	++	3	++	2	+	7	+	4-8	+	7	neg	7	++	4-8	++	3	+	9
19	++				+	7	+	4-8	+	4	+	7	++	4-8			++	9
20	+	3	++	3	++	7			++	4			+	4-8	++	3	++	4-9
21	+	4	++	3	+	7			+	9			+	5-8			+	5
22	trace	5	++	7	+	7			++	4			+	3-8	++	3	+	4-9
23	+		+	4	+	7			++	9			+	9	++	3	++	4-8
24	+		+	4	+	7			++	4-9			+	3-8	++	3	neg	4-8
25	trace	4-8			++	7			+	4-9			++	4-8			++	4-9
26	+	4	+	7	++	7			+	4			++	4-8	++	4	+	7
27	trace		+	4	+	7			+	4			neg	4-9	++	4	+	7
28	+	4-8	+	7	+	7			neg	7			+	4-9	++	4	neg	8
29	trace	4-8	+	4	++	7			neg	7			++	9	++	4	+	9
30	trace	7	+	4	++	7			neg	7			++	9	++	4	+	9
31	neg	3			+	7			+	7			++	5-9	++	4	neg	9
32	neg	3	+	4	+++	7			neg	7			neg	5-9	++	4	+	3-8
33	trace	3	++	7	++	7	++		+	7			neg	5-9	++	4	+	6-9
34	trace				+	7			+	7-9			+	5-9			+	5-9

It can be seen in the table that an acidic spot was often detected near one giving an alkaline reaction (see Probes 5, 8, and 10). There was no direct correlation between acidity and sulfide but in many cases alkalinity was associated with the absence of sulfide. This would be consistent with the hypothesis that the sulfur-containing salts such as $K_2S_2O_7$ and $KHSO_4$ produce the sulfide. Furthermore, the pH values were lower for the longer time exposures - i.e., Runs 9 and 2.

The alkaline areas are probably associated with deposits of K_2O or Na_2O which transform to their corresponding hydroxides in the presence of water.

Electron-Microprobe Analyses

The electron microprobe is an instrument which permits examination of a surface to determine the location and relative concentration of individual elements. This technique was used to examine the area at the scale-base metal interface on sections cut from corroded portions of boiler tubes removed from the Oceanside incinerator in 1968, 1969, and 1970. Sections from Miami County Corrosion Probes 2 and 3 were also examined, as were sections of Probe 10 from Norfolk, Virginia. None of these specimens were descaled prior to sectioning so that the areas could be viewed with some scale intact, but with the bulk deposit removed.

An illustration of the types of data obtained is provided in Figure 19 for a 1968 Oceanside tube. The position and intensity of the white areas in the photographs indicate the location and concentrations of the individual elements. This figure shows the relative concentrations of zinc, chlorine, tin, lead, copper, iron, potassium, and calcium in the scale and at the metal/scale interface. The base metal is located in the lower portion of the photographs, and the interface is at the rough-appearing area shown in the image photographs and indicated by the lines at the right side of the figure. The chlorine, zinc, and copper are found directly adjacent to the metal surface. In fact, some selective penetration of the zinc and chlorine into corroded areas of the metal is indicated at the pitted-appearing center area. The sulfur in this instance as in many others is concentrated in the deposit in a layer somewhat removed from the metal-deposit interface.

The microprobe results for the 18 specimens examined are summarized in Table 6.

The column designated 'inner layer' represents the interface between metal and adherent scale, while that designated the 'outer layer' is in the scale, slightly removed from the metal surface (approximately 2 mils). They both are beneath what is normally considered as deposit. In summary, all three Oceanside boiler tubes showed high concentrations of chlorine at the interface, and the 1968 and 1969 samples also had high concentrations of zinc in that region. The large amount of iron represents metal that diffused outward from the original tube surface in the form of corrosion products. Other unusual features are the large amounts of potassium in the inner layer of the 1969 sample, and high copper for the 1968 sample. Sulfur was found to be high only in the outer layer of the 1968 tube, as was lead. Potassium, calcium, and aluminum were concentrated in the outer layers of the deposits.

TABLE 6. RESULTS OF MICROPROBE ANALYSES

Element Layer	Relative Concentration of Elements																											
	Chlorine		Sulfur		Lead		Zinc		Iron		Copper		Sodium		Potassium		Calcium		Aluminum		Silicon		Tin		Nickel		Chromium	
	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer
Oceanside boiler tube, 1968	H	M	M	H	L	H	H	M	H	H	H	L	–	–	M	H	VL	H	–	–	–	–	L	L	–	–	–	–
Oceanside boiler tube, 1969	H	H	L	M	L	M	H	VH	H	M	M	L	VL	L	H	VH	VL	M	L	M	–	–	VL	VL	–	–	–	–
Oceanside boiler tube, 1970	H	L	M	VL	L	L	L	L	H	VL	L	L	–	–	–	–	–	–	L	H	–	–	–	–	–	–	–	–
Miami County Probe 2, A106B, 630 F	L	M	M	H	L	H	VL	L	VH	VL	–	–	VL	L	L	H	VL	L	L	L	L	M	L	L	–	–	–	–
Miami County Probe 2, T11 steel, 680 F	H	L	L	L	L	L	L	L	VH	VL	–	–	L	L	L	H	L	H	M	L	VL	H	–	–	–	–	M	VL
Miami County Probe 2, 304 stainless, 1130 F	L	L	L	VL	L	L	L	M	VH	VL	–	–	–	–	M	L	L	M	L	M	L	H	–	–	H	VL	H	VL
Miami County Probe 2, 321 stainless, 1150 F	L	L	M	L	L	L	M	M	VH	H	–	–	–	–	L	L	VL	M	L	M	M	H	–	–	H	M	VH	L
Miami County Probe 3, A106B steel, 300 F	H	H	L	L	L	H	M	L	VH	H	H	M	L	L	H	M	–	–	–	–	–	–	–	–	–	–	–	–
Miami County Probe 3, A106B steel, 450 F	M	L	H	L	–	–	VH	L	VH	L	–	–	–	–	M	L	–	–	M	VH	–	–	–	–	–	–	–	–
Miami County Probe 3, A106B steel, 820 F	L	M	H	VL	M	H	H	VL	VH	VL	–	–	L	L	H	VL	–	–	L	H	–	–	L	L	–	–	–	–
Miami County Probe 3, T11 steel, 500 F	H	L	H	VL	H	L	H	M	H	VL	–	–	L	L	VH	L	–	–	L	VH	–	–	–	–	–	–	VH	M
Miami County Probe 3, 321 stainless, 1005 F	H	M	L	H	–	–	–	–	VH	H	–	–	L	L	L	H	L	M	–	–	–	–	–	–	VH	VH	L	VL
Norfolk, Va. Probe 10, T11 steel, 340 F	M	H	VL	L	L	M	M	M	VH	VH	–	–	–	–	H	VH	–	L	VL	VL	M	M	M	M	–	–	–	–
Norfolk, Va. Probe 10, A106 steel, 440 F	L	L	–	–	–	–	VL	M	M	H	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Norfolk, Va. Probe 10, 321 stainless, 540 F	M	M	L	M	L	M	M	M	VH	L	–	–	–	–	H	M	–	–	VL	M	VL	M	L	L	H	VL	VH	VL
Norfolk, Va. Probe 10, A106 steel, 660 F	M	M	VL	VL	–	–	H	M	VH	VH	–	–	–	–	L	L	–	–	–	–	–	–	–	–	–	–	–	–
Norfolk, Va. Probe 10, A106 steel, 750 F	L	L	M	H	VL	M	H	H	VH	VH	–	–	VL	VL	H	H	–	–	VL	VL	VL	VL	L	L	–	–	–	–
Norfolk, Va. Probe 10, 321 stainless, 805 F	L	M	H	H	VL	H	L	H	VH	L	–	–	–	–	L	H	–	–	L	M	VL	L	L	L	VH	VL	VH	VL

Note: VH – very high, H – high, M – moderate, L – low, VL – very low. Dash indicates element not found in image area.

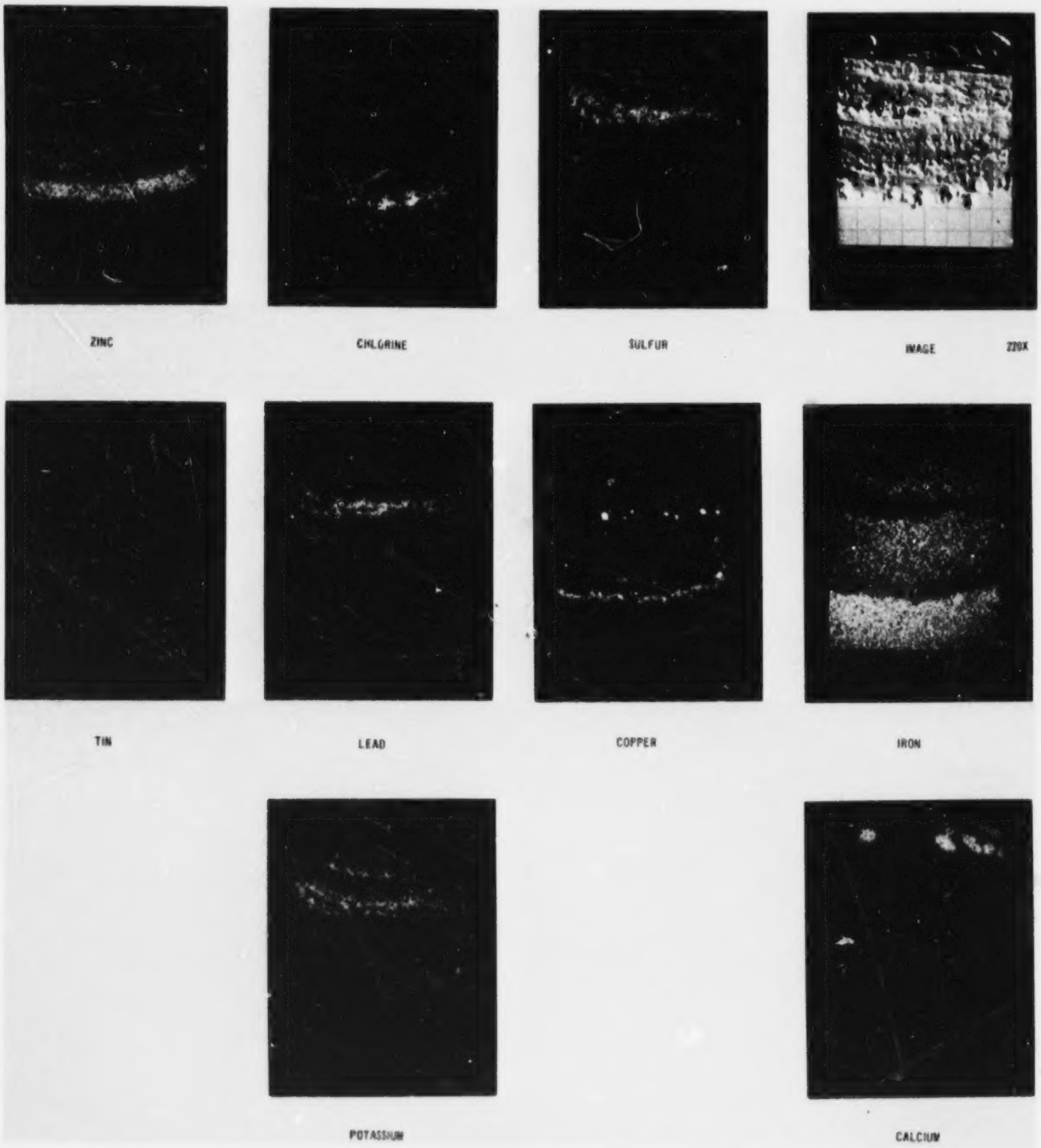

ZINC
CHLORINE
SULFUR
IMAGE 220X
TIN
LEAD
COPPER
IRON
POTASSIUM
CALCIUM

FIGURE 19. RELATIVE CONCENTRATIONS OF SELECTED ELEMENTS IN METAL-DEPOSIT INTERFACE OF CORRODED BOILER TUBE REMOVED FROM OCEANSIDE INCINERATOR IN 1968

Electron-Microprobe Pulse-Mode Photographs.

For the corrosion-probe specimens exposed in the Miami County incinerator, chlorine was high at the inner layer for four of the nine specimens examined and was present on the remaining ones. Similarly, sulfur was high on three pieces and was present on the other six. Potassium, aluminum, zinc, and lead were also found in large amounts on many of the pieces. Copper was found only on Probe 3, the 300-F specimen.

In general, the chlorine was less concentrated on the specimens from the Norfolk Probe 10. It was present on all six pieces examined, but was high only in the outer layer of the 340-F specimen. Sulfur was present in large amounts on the specimens from 750 and 805-F positions, but was absent on the 440-F specimen. Zinc was present on all six specimens and was high on three of them. Smaller amounts of lead were found. Potassium was high on half of the specimens.

Potassium, chlorine, and sulfur were found deep within a grain boundary on the 540-F specimen, a Type 321 steel.

The microprobe results show that compounds containing zinc, potassium, chlorine, sulfur, and sometimes lead are usually present at the corroded tube surfaces. Thus, these results coupled with X-ray studies and laboratory experiments with various salts help impart an understanding of the cause of the corrosion. This point is discussed more fully later.

X-Ray Diffraction Studies

Since chemical assays have revealed that a large number of elements are retained in the deposit extracted from air-cooled probes of refuse incineration, and since electron-microprobe analyses have shown several of these elements to be concentrated in the adhering scale, phase studies have been conducted to determine how these elements are combined. The phase studies have been conducted by obtaining X-ray-diffraction data on the bulk deposit and on the individual layers revealed by microscopic examination. Figure 20 presents typical analyses for various probe temperatures and a photomicrograph illustrating the general location and appearance of the scale and deposit as seen under reflected light. The colors indicated in the tabulation were determined under oblique illuminations from an incandescent lamp. It is evident from these results that distinct phase changes occur at various distances from the tube-metal surfaces as well as at different probe temperatures.

It can be seen first, that unlike the normal oxidation of iron which results in a layer sequence Fe-FeO-Fe_3O_4-Fe_2O_3 above 1040 F, or Fe-Fe_3O_4-Fe_2O_3 below 1040 F, the scale in contact with the substrate metal is found to contain $FeCl_2$-$2H_2O$ throughout the entire probe-temperature range 300 to 1200 F. The hydrate form of $FeCl_2$ undoubtedly resulted from exposure to humid air after the probe was removed; in the incinerator the form is probably $FeCl_2$. At the moderately high temperature end of the probe, it was found that the $FeCl_2$ layer melts and collects into small pools. As can also be seen in Figure 20, a layer of FeS was also found on specimens from the high-temperature end of the probe.

The electron microprobe showed that some zinc compound was also present in this area near the metal. It appears that this element is not in a form readily detected

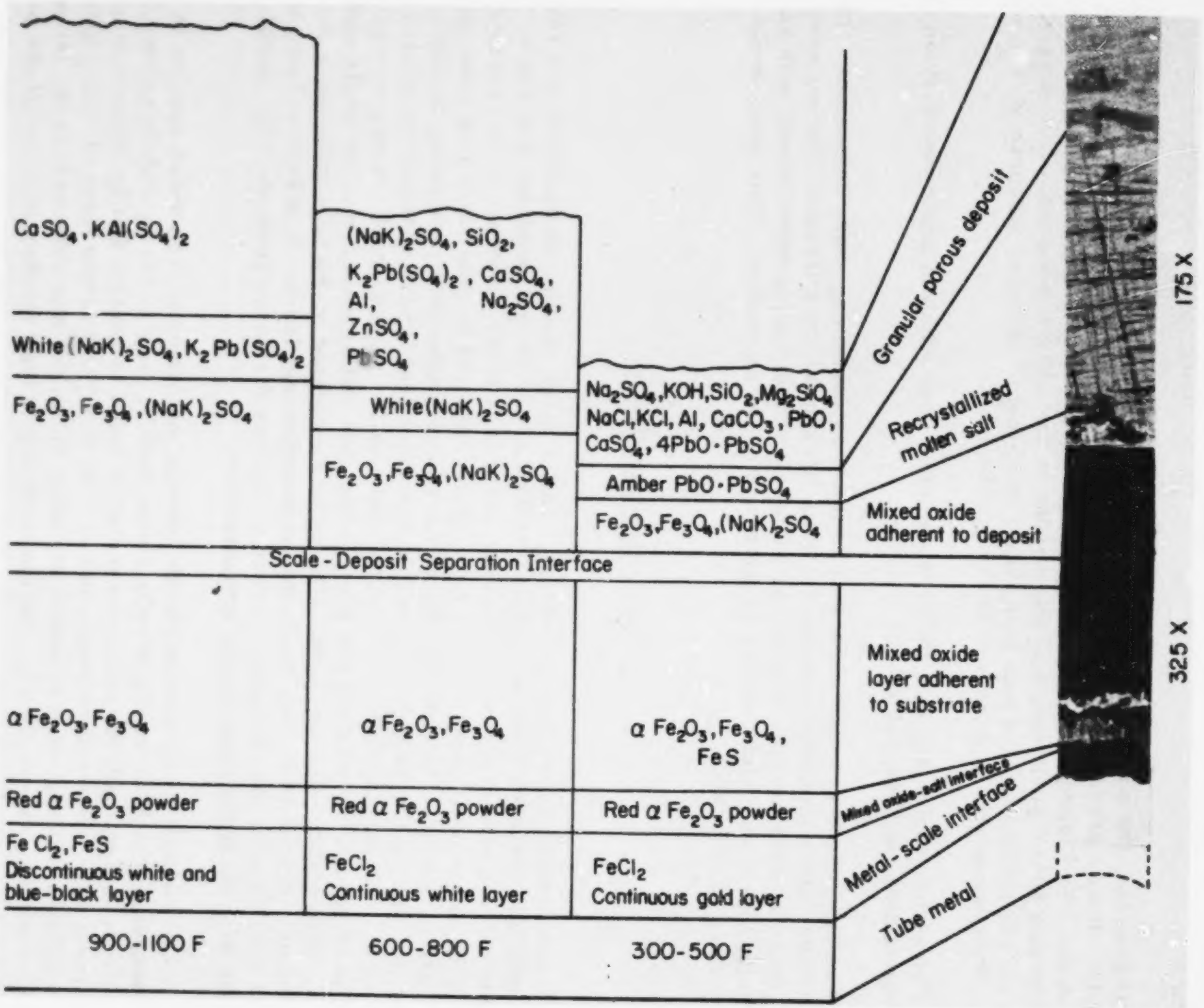

$CaSO_4$, $KAl(SO_4)_2$
White $(NaK)_2SO_4$, $K_2Pb(SO_4)_2$
Fe_2O_3, Fe_3O_4, $(NaK)_2SO_4$
$(NaK)_2SO_4$, SiO_2, $K_2Pb(SO_4)_2$, $CaSO_4$, Al, Na_2SO_4, $ZnSO_4$, $PbSO_4$
White $(NaK)_2SO_4$
Fe_2O_3, Fe_3O_4, $(NaK)_2SO_4$
Na_2SO_4, KOH, SiO_2, Mg_2SiO_4, NaCl, KCl, Al, $CaCO_3$, PbO, $CaSO_4$, $4PbO \cdot PbSO_4$
Amber $PbO \cdot PbSO_4$
Fe_2O_3, Fe_3O_4, $(NaK)_2SO_4$
Scale - Deposit Separation Interface
α Fe_2O_3, Fe_3O_4
α Fe_2O_3, Fe_3O_4
α Fe_2O_3, Fe_3O_4, FeS
Red α Fe_2O_3 powder
Red α Fe_2O_3 powder
Red α Fe_2O_3 powder
$FeCl_2$, FeS
Discontinuous white and blue-black layer
$FeCl_2$
Continuous white layer
$FeCl_2$
Continuous gold layer
900-1100 F
600-800 F
300-500 F
Granular porous deposit
Recrystallized molten salt
Mixed oxide adherent to deposit
Mixed oxide layer adherent to substrate
Mixed oxide-salt interface
Metal-scale interface
Tube metal
175 X
325 X

FIGURE 20. SCHEMATIC LOCATION OF PHASES IDENTIFIED BY X-RAY DIFFRACTION

by X-ray techniques, but may be incorporated in the $FeCl_2$ as (Fe, Zn)Cl_2 or in the FeS as (Fe, Zn)S with the host structures. Lattice-parameter data were not obtained, but shifts in line position were observed from specimen to specimen.

These interface layers are of the order of 6 to 10 microns thick on the low temperature specimens. The thickness increases somewhat with temperature.

Between the interface scale and the bulk deposit is a multilayered scale of iron oxides: Fe_2O_3 and Fe_3O_4. It is interesting to note that a thin layer of alpha Fe_2O_3 forms at the $FeCl_2$-mixed oxide interface. Part of the mixed-oxide scale adheres to the substrate and part to the external deposit. The mixed-oxide (Fe_2O_3-Fe_3O_4) layer is a hard, brittle, magnetic, gray-black material which thickens with temperature and is made up of several layers with loose red Fe_2O_3 between layers. This suggests that reduction or reaction with other elements occurs in or below this layer as is discussed later. At the higher temperature where FeS forms, the mixed oxide scale is less adherent, and in this area, more of the mixed oxide is removed with the outer deposit. The topography of the corroded metal here changes from relatively smooth to dimpled.

Now as one examines the phases present in the deposit up and beyond the separation line shown in Figure 20, it can be seen that a great number of compounds have been identified by X-ray diffraction. These compounds have been arranged in classes and are listed below along with the compounds found near the tube.

$PbSO_4$
$ZnSO_4$
Na_2SO_4
$(Na, K)_2SO_4$
$CaSO_4$
$K_2Pb(SO_4)_2$
$KAl(SO_4)_2$

SiO_2
αFe_2O_3
Fe_3O_4
PbO
PbO· $PbSO_4$
4PbO· $PbSO_4$

NaCl
KCl
$FeCl_2$

$CaCO_3$
Al
KOH
Mg_2SiO_4
FeS

It should be mentioned that the examinations with the microscope indicated that some melting had occurred near the scale. These studies showed the presence of recrystallized continuous phases $(NaK)_2SO_4$ and PbO· $PbSO_4$ on the external surface of the mixed iron oxide scale. The $(NaK)_2SO_4$ phase is also dispersed throughout the iron oxide scale that adheres to the bulk deposit. It appears that separation in the iron oxide scale occurs at the depth to which this salt phase has permeated in sufficient quantity to destroy the integrity of the iron oxide. It is proposed that in the initial stage of incinerator operation, these salt phases as well as mixed chloride salts possibly $ZnCl_2$ and $PbCl_2$ permeate the iron oxide scale and destroy its protective characteristics.

As is discussed later, these salt phases when molten also contribute to maintaining a low oxygen partial pressure in the adherent scale. While the melting points even for mixtures are significantly higher than those indicated by thermocouples placed in the metal probes, the furnace-gas temperature will be much higher than the temperature of the probe because of the thermal gradient in the deposit. This condition is substantiated by the fact that molten pools of $FeCl_2$ were detected where no deposit had formed on a high-temperature (1100 F) probe sample, but did not melt on the opposite side of the same section where the deposit had formed. It is interesting to note that the molten salt at the deposit-mixed oxide interface changes color and phase with time and temperature. In short times the deposit consists of NaCl, KCl and an unidentified phase containing large quantities of Zn or Pb while for longer exposures the melted deposit on low-temperature sections (~300 F) was found to be $PbO \cdot PbSO_4$, at intermediate temperature Na_2SO_4 plus KOH and at high temperatures $(NaK)_2SO_4$ plus K_2PbSO_4.

CORROSION FROM INCINERATOR DEPOSITS UNDER HUMID CONDITIONS

Stress-Corrosion Cracking

Since all incinerators must be shut down on occasion, and since high humidity conditions can often cause the deposit on the tube surfaces to become moist, it is important to assess the severity of attack under these conditions. The most damaging forms of attack to be anticipated are stress-corrosion cracking (SCC) and pitting. Probably the most hazardous of these is stress-corrosion cracking.

When an alloy is simultaneously subjected to surface-tensile stresses and a variety of specific corrosive environments, it may experience premature failure because of stress-corrosion cracking. This process is unique in that failure does not occur when the individual factors mentioned above are acting alone.

One aspect of the phenomenon is that the metal at the failed areas does not exhibit ductile tearing, but instead exhibits a brittle fracture. Crack propagation, once initiated, is quite rapid. The propagation is in a plane perpendicular to the direction of the applied stress. The cracks may be either transgranular or intergranular, depending on the alloy and the composition of the environment.

The tensile stresses required for cracking may be either applied or residual. The latter may result from welding or from press fits or other assembly procedures. Also, the presence of crevices may favor the initiation of stress-corrosion cracks.

All common structural materials such as carbon steel, low-alloy steels, stainless steels, aluminum alloys, copper alloys, and nickel alloys are susceptible to SCC to varying degrees in some specific environments. The mechanism of the cracking is not completely understood. From an engineering standpoint, however, it is important to know which combinations of materials and environments will initiate cracking.

Mild steels will crack in certain nitrate, caustic, and carbonate-bicarbonate aqueous solutions and in some gaseous CO-CO_2-H_2O mixtures, anhydrous ammonia, and H_2S-containing environments. Obviously, these substances cannot all be avoided in incinerators. It is considered unlikely, however, that the specific combinations of these substances which promote SCC of mild steel will be encountered in incinerators except on rare occasions. Aqueous nitrates and gaseous CO-CO_2-H_2O mixtures would be the most likely causes of SCC in mild-steel incinerators.

While SCC of stainless steels can occur in caustic environments, the most important substance promoting the SCC of stainless steels is chloride ion. Trace quantities of this substance are enough to cause austenitic stainless steels to develop stress-corrosion cracks rapidly. While higher temperatures generally favor SCC, Type 304 will crack even at room temperature.(34) Stainless steel alloys will crack when stressed to as low as 2000 psi in the presence of a few parts per million of chloride ions.(35)

Since chloride ions are commonly present in incinerator deposits, two groups of materials were evaluated for SCC while in contact with incinerator deposit under humid conditions. The first group of alloys included Types 304, 310, and 446 stainless steels and carbon steels A106, Grade B, and A213, Grade T-11. The Group 2 specimens included Type 316L stainless steel and three other alloys more resistant to SCC in chloride environments, namely, Inconel 600, Inconel 601, and Incoloy 825. Bent specimens (C-rings) were stressed to a level halfway between the yield stress and the ultimate tensile strength (at the SCC test temperature). Some U-bend configurations were also used. Some specimens of Type 304 stainless steel were sensitized for 2-1/2 hours at 1200 F to increase their susceptibility to SCC. Other specimens were tested as received.

The tensile-stressed surface of the specimens was exposed to incinerator deposit in a moist-air atmosphere at about 170 F. Group 1 specimens were exposed to deposits from Miami Probe 3, Samples 1 through 8, or Probe 4, Samples 1 through 7. Group 2 specimens were exposed to deposits from Miami Probe 12, Samples 1, 2, and 3.

The apparatus for these moist-air SCC experiments is similar to a double boiler: the specimens are placed on dry pulverized incinerator deposit in the inner vessel while distilled water in the outer vessel is heated to humidify the atmosphere.

In the Group 1 alloys, the Type 304 specimens (both sensitized and annealed) showed cracks after an exposure of one week. Fracture occurred on the sensitized Type 304 piece during the eighth week of exposure. Cracks were first observed in Type 310 steel after 10 weeks. Deep stress-corrosion cracks developed in all three materials during 20 week's exposure. There were fewer cracks on the Type 310 specimens but they were very deep. The attack on this material was predominantly transgranular as is illustrated in Figure 21.

The nature of the cracking on Type 304 stainless steel at the end of three weeks is illustrated in Figure 22. That metallographic examination of cracked specimens of Type 304 revealed a number of branching cracks in both specimens. The cracks in the unsensitized specimen follow a predominantly transgranular mode of propagation; that is, most cracks cut through grains. The sensitized specimen, however, revealed a considerable degree of intergranular propagation of cracks.

On the other hand, no SCC has been observed with Type 446 steel after 22 weeks of exposure. The specimen, however, was quite rusty and pitted. After 12 weeks, the A106 and T-11 steels were quite rusty and scaled but no stress-corrosion cracking was observed. The surface roughening on these steels was noticeable at 15X but was not great. There was no indication of deep pitting as is sometimes seen in corrosive environments.

The Group 2 alloys were exposed for 26 weeks. Only the Type 316L specimens exhibited cracking and this was at 22 weeks. However, some rusty appearing spots appeared on this specimen in about four weeks. As can be seen in Figure 23, the cracking started at one of the rusty areas. A photomicrograph taken of a section cut through the crack indicates that the attack is transgranular in nature.

At 26 weeks, the Inconel 601 specimen showed many fine, shallow pits. Some of these appeared at four weeks as rusty spots.

The Inconel 600, at 26 weeks, was mottled in appearance as if it were etched in spots. This alloy also showed a few rusty spots after four weeks.

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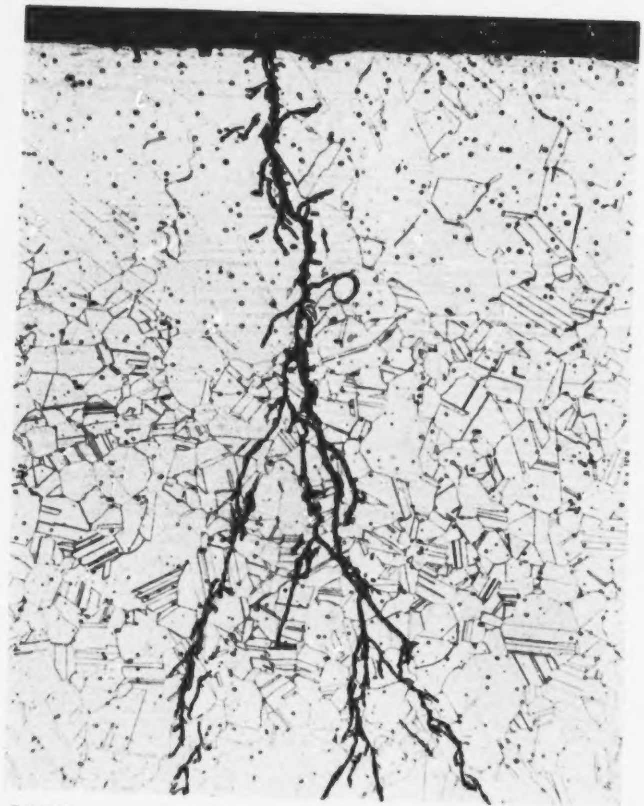
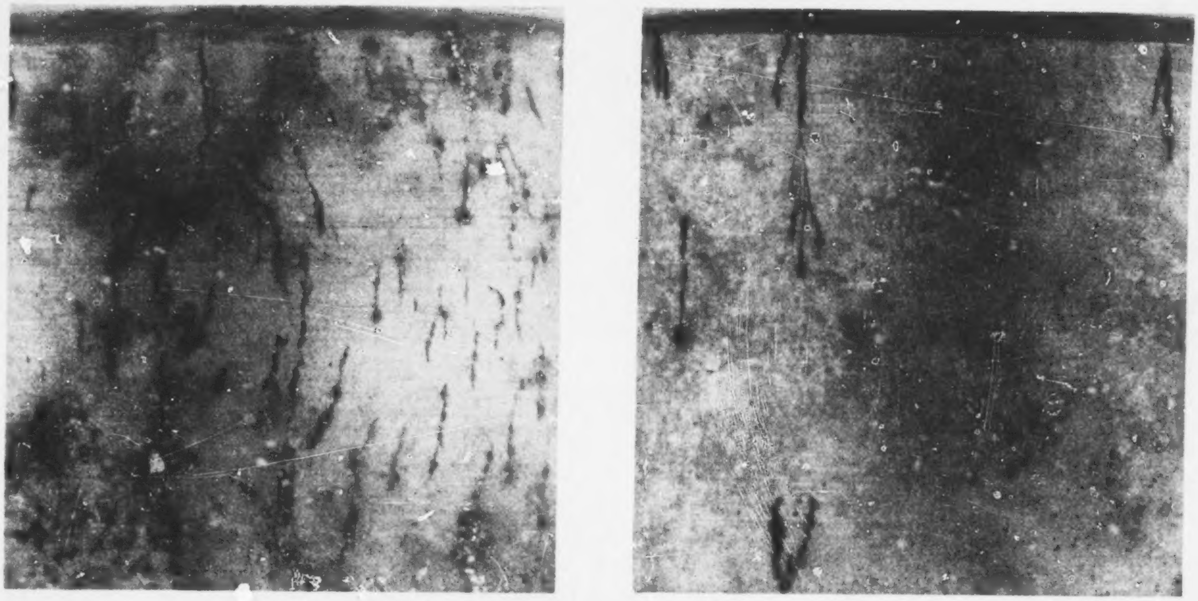


FIGURE 21. STRESS CORROSION CRACK IN C-RING OF TYPE 310 STAINLESS STEEL EXPOSED TO INCINERATOR DEPOSIT UNDER HUMID CONDITIONS

The cracking is largely transgranular.

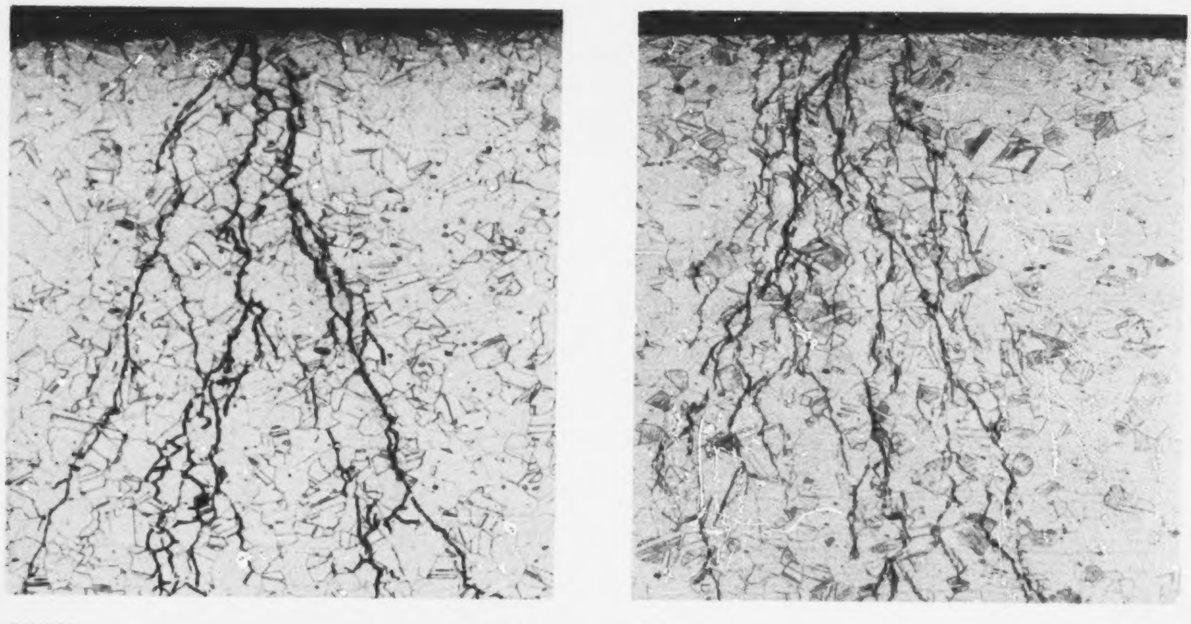


7X C-3937

a. Sensitized 2-1/2 Hours at 1200 F

7X C-3938

b. Unsensitized



100X C-3939

c. Photomicrograph of Sensitized Specimen

100X C-3940

d. Photomicrograph of Unsensitized Specimen

FIGURE 22. STRESS-CORROSION CRACKS RESULTING FROM EXPOSURE OF STRESSED TYPE 304 STAINLESS STEEL TO MOIST INCINERATOR DEPOSIT AT 170 F

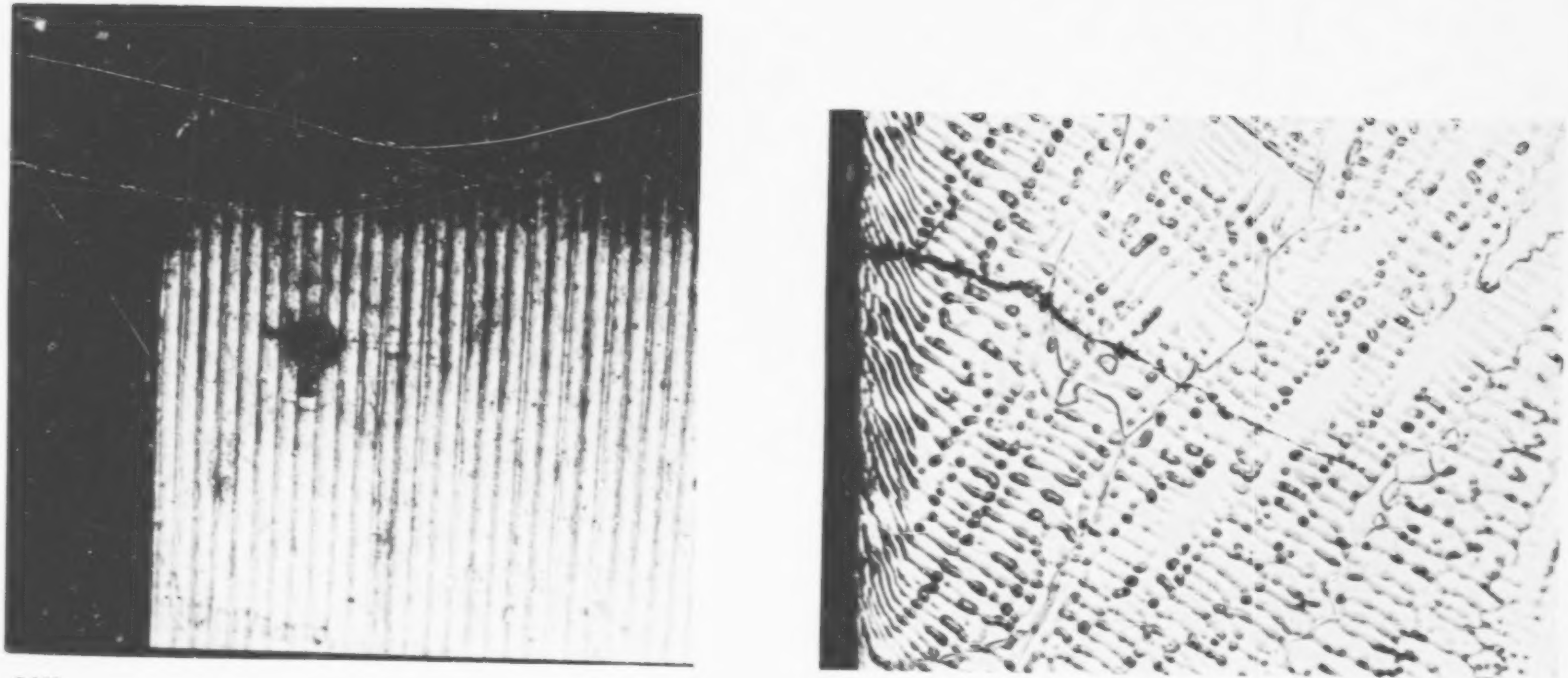

20X
C4010
250X
C4011

FIGURE 23. SCC IN C-RING OF TYPE 316L STAINLESS STEEL AFTER EXPOSURE TO INCINERATOR DEPOSIT UNDER HUMID CONDITIONS

The crack initiated at a pit.

The Incoloy 825 showed good resistance throughout the 26-week period. It is, therefore, concluded that this alloy is a good choice when resistance to downtime conditions is considered. Since the steels A106, Grade B; and A213, Grade T-11 are corroded in a fairly uniform manner under these conditions, they can also be considered for construction materials. The relatively good performance of the tubes in the boiler at the Navy Public Works Salvage Fuel Boiler provides additional evidence for consideration of carbon steels.

The austenitic-type stainless steels such as 304, 310, 316, etc., do not appear to be good choices because of the likelihood of the incidence of stress-corrosion cracking.

The ferritic-type stainless steels as exemplified by 446, have the limitation of possibly being subject to severe pitting under the downtime conditions.

Apparently, these laboratory conditions were more severe than those experienced in the field because the corrosion probe specimens exposed at Miami County did not show bad pitting even when downtime occurred weekly.

Ferritic steels like Type 446 are thought to be immune to SCC in chloride media, but they may be embrittled by hydrogen, particularly when sulfur is present.(36)

Stressed C-ring specimens of Types 304, 310, and 446 steel have also been exposed to pulverized incinerator deposit at 1000 F for 50 and 250 hours in a simulated incinerator atmosphere containing HCl and SO_2. As expected from previous work,(37) none of the four stainless steel specimens developed any evidence of SCC under these conditions. However, all four specimens were severely corroded on the surfaces that contacted the deposit. A later section of this report gives the corrosion rates for pieces exposed with the C-rings.

Other stressed C-ring specimens were exposed at 1000 F for 50 and 250 hours to a salt mixture of 29.6 g K_2SO_4 + 0.3 g NaCl in the same gaseous environment. This environment was selected because it borders test results with high and low corrosion rates and, accordingly, it would be more likely than most of the other environments investigated to induce SCC. Again, none of the specimens developed stress-corrosion cracks, although all were somewhat tarnished on surfaces that contacted the salt.

Additional stressed C-ring specimens were exposed to the simulated incinerator atmosphere (as above) but in the absence of contact with either salt mixture or incinerator deposit. Neither cracking nor much corrosion attack resulted from these exposures.

Metallographic examination of specimens exposed to hot salts and incinerator deposits revealed some instances of surface-layer intergranular attack, but no evidence of SCC.

The results of these investigations confirm that SCC is not likely to be a problem with stainless steels at the operating temperatures of incinerators. However, as was shown previously, the damp incinerator deposits can cause cracking.

LABORATORY CORROSION STUDIES

The objective of the laboratory experiments was to determine the importance of individual factors on corrosion in incinerators and also to help establish the mechanism by which metal wastage occurs. Since the experiments could be carried out under carefully controlled conditions, it was possible to determine the role of such factors as gaseous components, salts, or deposits, metal composition, and temperatures. The analyses made by the microprobe, X-ray, and analytical chemistry have served to define corrosive salt mixtures to be studied.

The approach taken in the research described was to subject alloys to simulated flue gases with and without direct contact with known salt mixtures. Weight losses were used to assess the amount of corrosion which occurred.

Apparatus and Procedures

Metal specimens were placed in porcelain boats or crucibles located within quartz or Vycor tubes passing through resistance-heated tube furnaces. Gases were preheated in a section which was packed with quartz wool to enhance heat transfer.

Synthetic furnace gases (FG), consisting of typical mixtures of CO_2, air, and water as encountered in the incinerator, were used with SO_2 and HCl separately and in combination. The standard composition used was: 80 percent air, 10 percent CO_2, and 10 percent H_2O with 250 ppm SO_2. The gas flow was about 0.16 cfm, which corresponds to a linear velocity of 0.2 fps. HCl was added on occasion in amounts of 200 and 2000 ppm.

The equipment upstream of the reactor consisted of flowmeters for metering carbon dioxide and air to the reactor, manometers to regulate the pressure of these two gases at 19.7 psia, and a manometer for determining pressure drop through the system and exit portion of the setup. The controlled and small amount of SO_2 was brought into the stream of carbon dioxide through capillary tubes. The flow of sulfur dioxide was determined and checked periodically by the hydrogen peroxide method. By sparging air through heated water, water vapor was introduced into the system and was controlled by the flow of air and the temperature of the water reservoir.

Corrosion specimens about 0.75 x 0.175 x 0.125 inch were made from A106 Grade B, A213 Grade T11, and Type 321 stainless steel.

Exposure times were usually 50 hours and the extent of corrosion was evaluated by weight-change measurements and by metallographic examinations. The sodium azide test described earlier was also used to detect the presence of sulfide on the corroded steel specimens.

Results

Gas-Phase Reactions

As might be expected, the attack of metals by gas-phase reactions was not great at normal operating temperatures – i.e., 800 F. Details of the extent of the attack from furnace gases containing 200 ppm HCl on A106 and T11 steel at 800, 1000, and 1200 F are summarized in Table 7. It can be seen that the corrosion rates increased rapidly as the temperatures increased in a manner similar to that noted on many incinerator corrosion probes although the estimated wastage of these laboratory specimens was much less than for the probe specimen. The presence of HCl had little effect on these corrosion rates.

TABLE 7. GAS-PHASE CORROSION AT ELEVATED TEMPERATURES

Alloy	Temperature	Corrosion Rate, mils per month
A106	800	0.9
A106	1000	8
A106	1200	36
T11	800	0.8
T11	1000	6
T11	1200	29

Sulfate-Chloride Mixtures at 1000 F

As was mentioned earlier in this report, chlorine- and sulfur-containing salts were found in deposits from the incinerator corrosion probes. Microprobe analyses of corroded surfaces from the same probes have shown that these salts are very near or adjacent to the bare metal surfaces. Thus, such salts can be suspected of being of importance from the corrosion standpoint.

Experience in oil- and coal-fired boiler furnaces has amply demonstrated the role of chlorine in fuels as an accelerating agent in corrosion processes.(38-42) Corrosion by mixed sulfate-chloride salts has been observed. However, most of the reported work had been done at temperatures above 1000 F and with alloy steels rather than with carbon steels.

Most of the work at 1000 F was carried out with a base corrosion mixture of K_2SO_4 and Na_2SO_4 in the molar ratio of 3 to 1.

Detailed conditions concerning the corrosion mixture composition and gas atmosphere along with wastage rates at 1000 F are summarized in Figure 24. The lower line on this figure also shows the results of the azide test for the presence of sulfide on the corroded metals. A triple +++ mark indicates a very strong test result. The corrosion is expressed in units of mils/month as calculated and extrapolated from the weight loss values for 50 hours of exposure.

As can be seen in Figure 24, Run 3, the K_2SO_4-Na_2SO_4 mixture with Fe_2O_3 added did not accelerate corrosion above that obtained in flue gas alone (Run O). However, when 1 percent NaCl was added, the corrosion was greatly increased as indicated in Runs 1, 5, and 20. Runs 5 and 20 were repeat runs and demonstrate fairly good reproducibility.

The addition of Fe_2O_3 was made to determine whether reactions to form alkali iron trisulfates took place. Such compounds are known to be corrosive at 1100 F. Since the addition did not accelerate corrosion, it was concluded that the corrosiveness of the mixture or the possible formation of alkali-metal ferric trisulfates from sodium and/or potassium sulfates, iron oxide, and sulfur trioxide was not of major concern in the temperature range used.

As shown by Run 7, K_2SO_4 with 1 percent NaCl was less corrosive than the mixture of K_2SO_4 and Na_2SO_4 with NaCl.

Increasing the chloride content had negligible effect although the action of KCl on A106 and T11 steels at 5 percent level seemed to be somewhat less than for NaCl. (Runs 10, 11).

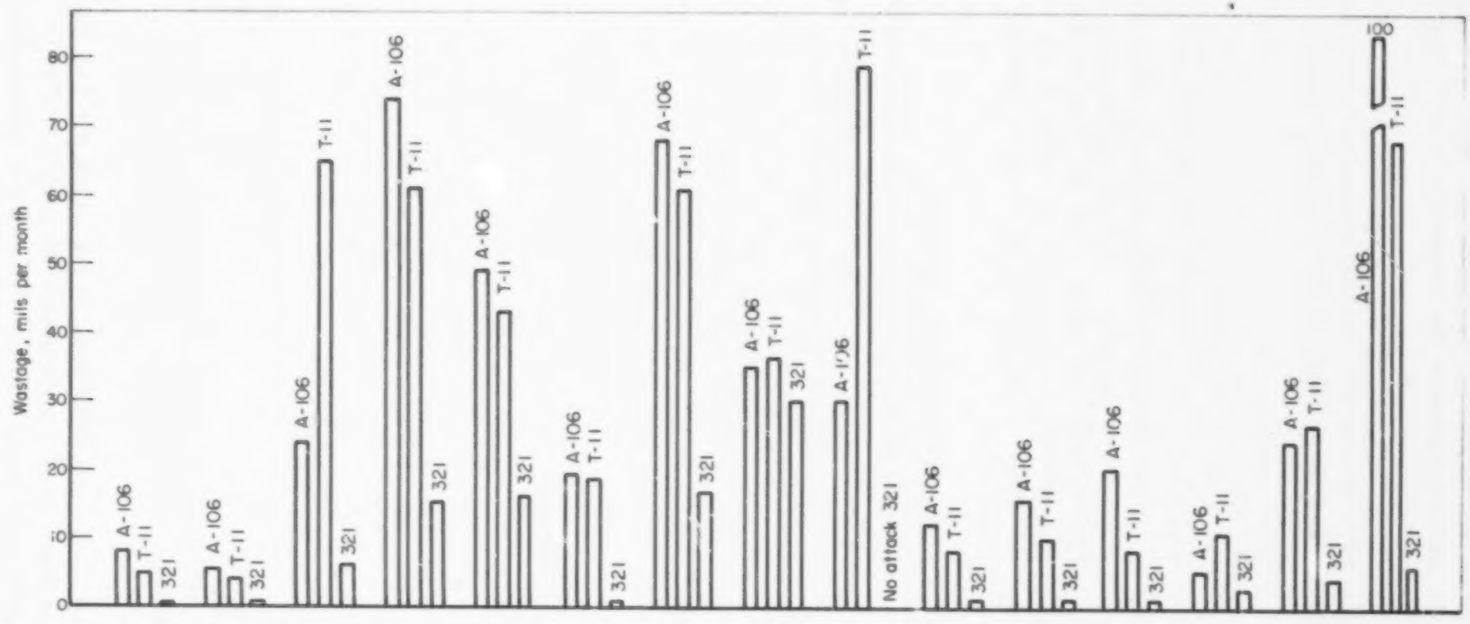
It is significant that sodium chloride alone in the presence of flue gas was quite corrosive to the carbon steels, i.e., Run 13 Of even greater significance is the fact that sulfide as revealed by the azide test, was found on these specimens. Thus, some reaction involving the SO_2 in the flue gas was of importance since that was the only source of sulfur. Sulfide had been detected, of course, in all preceding runs in which corrosion had occurred. There was also a correlation between the severity of corrosion and the amount of sulfide detected.

In order to get a better understanding of the possible reactions involving sulfur and SO_2, several experiments were conducted with SO_2 eliminated. In addition, experiment No. 21 was carried out where the SO_2 content of the flue gas was increased from 250 to 2500 ppm.

As can be seen from Runs 15, 16, and 18, the elimination of SO_2 from the flue gas decreased markedly the corrosion for chloride alone and for sulfate-chloride mixtures. Runs 16 and 18 were repeat experiments and it can be seen that results are in quite good agreement. It is important to note that no sulfide was detected on the metal surfaces of the specimens for the three runs just mentioned, i.e., with SO_2 absent.

Similarly the corrosion was low and no sulfide was formed when the exposures were carried out under helium with no SO_2 present (Run 17). The addition of SO_2 (2500 ppm) to the helium increased the corrosion several times as indicated for Run 19. No sulfide was detected on these specimens.

In the experiment with the synthetic flue gas containing 2500 ppm SO_2 (Run 21), a slight increase in corrosion rate was measured on the A106 steel, but the corrosion rates on the T11 steel specimens were comparable to those when the level of SO_2 in the gas was 250 ppm (Run 10).



Run	0	3	1	5	20	7	10	11	13	15	16	18	17	19	21
K_2SO_4 %	–	59	58	78	78	99	75	75	–	–	78	76	78	78	75
Na_2SO_4 %	–	16	16	21	21	–	20	20	–	–	21	21	21	21	20
NaCl %	–	–	1	1	1	1	5	–	100	100	1	1	1	1	5
Misc. %	–	25 Fe_2O_3	25 Fe_2O_3	–	–	–	–	5 KCl	–	–	–	–	–	–	–
Atmosphere	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	No SO_2	No SO_2	No SO_2	Helium	He + SO_2	F.G. Hi SO_2
Azide test	–	?	++	+++	++	+	+++	+++	+++	–	–	–	–	–	+++

FIGURE 24. LABORATORY CORROSION RESULTS AT 1000 F

Exposure time was 50 hours.

In other experiments it was found that extremely rapid attack of Type 321 stainless steel resulted from lead chloride at temperatures near 1000 F. Metallographic studies revealed intergranular penetration in addition to the general attack. The alloy was also attacked by molten zinc and zinc chloride vapor.

The A106-Grade B and low-alloy A213-Grade T11 carbon steels were attacked about five times more rapidly at 1000 F when lead chloride was present than when it was absent.

Incinerator Deposits

A few experiments were carried out in the laboratory using deposits taken directly from the Miami County corrosion probes. For comparison, exposure tests were conducted in synthetic furnace gas only and in Na_2SO_4 containing 1 percent NaCl. Results are summarized in Table 8. The corrosion which occurred is expressed, first, as a weight loss in milligrams; second, as penetration in mils; and third, as a rate in mils per month.

TABLE 8. LABORATORY CORROSION STUDIES WITH INCINERATOR DEPOSITS

Chemical Environment	Units of Corrosion	Steel Type						
		310	S304	304	446	A106	T11	321
	Run 60 – 50 Hours at 1000 F							
Gas only[a]	Wt loss, mg	0.1	2.8	3.4	8.2			
Na_2SO_4 + 1 % NaCl in furnace gas	Wt loss, mg	6.3	9.0	39.5	10.6			
	Penetration, mils	0.07	0.1	0.45	0.12			
	Rate, mils/month	1.0	1.5	6.6	1.8			
Deposit from Probe 3 in furnace gas	Wt loss, mg	348	417	411	375			
	Penetration, mils	3.9	4.8	4.7	4.3			
	Rate, mils/month	57	70	70	63			
	Run 61 – 250 Hours at 1000 F							
Gas only[a]	Wt loss, mg	1.0	8.4	12.7	11.9			
Na_2SO_4 + 1 % NaCl in furnace gas	Wt loss, mg	9.1	24.3	104	34.8			
	Penetration, mils	0.1	0.3	1.2	0.4			
	Rate, mils/month	0.3	0.9	3.6	1.2			
Deposit from Probe 3 in furnace gas	Wt loss, mg	950	953	994	775	1296	1586	
	Penetration, mils	10.8	10.8	11.3	8.8	14.7	18.0	
	Rate, mils/month	31	31	33	26	43	52	
	Run 63 – 50 Hours at 1000 F							
Very low temperature deposit from Probe 9 in furnace gas	Wt loss, mg					219	80	14.5
	Penetration, mils					1.0	0.4	0.07
	Rate, mils/month					15	5.9	1.0

(a) 80 % air, 10 % CO_2, 10 % H_2O, 250 ppm SO_2, 2000 ppm HCl.

Runs 60 and 61 were conducted for 50 and 250 hours, respectively. The deposit mixture for these runs was a portion taken from Specimens 1 through 8 of Probe 3. It can be seen in Table 7 that the incinerator deposit was much more corrosive than was the Na_2SO_4-NaCl mixture or the furnace gas alone. It is also evident that the corrosion rate was greater for the 50-hour exposure than for the 250-hour exposure. This corresponds to the observation discussed for the field work in that the corrosion appeared to decrease with increasing times of exposure. The results also show greater attack in the A106 and T11 steels than on the stainless steels, as would be expected. Results, in general, agree fairly well with those obtained in the field.

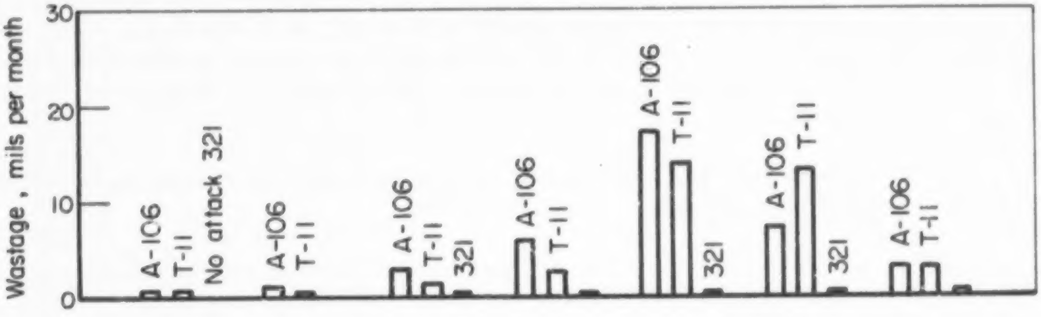
The deposit sample used in Run 63 was taken from the water-cooled section of Probe 9. The corrosion resulting from this deposit was much less than that from the deposit taken from Probe 3.

These experiments were carried out at the same time as the stress-corrosion-cracking studies discussed elsewhere in this report.

An oily liquid collected at the cool end of the furnace tube during these experiments. This liquid was quite acidic and analysis showed it to be H_2SO_4. It is believed that compounds such as pyrosulfates or bisulfates in the deposits are being thermally decomposed during the heating to release SO_3, which then combines with moisture to form H_2SO_4. In experiments with bisulfates and pyrosulfates described later, a similar liquid condensed at the exit by the furnace tube, particularly when bisulfates were heated.

Corrosion at 800 F

Seven experiments were carried out at 800 F under conditions similar to those discussed in the series at 1000 F. Results are summarized in Figure 25. In general, the accelerating effect of NaCl can be seen although wastage rates are much lower than at 1000 F. The effect of varying the SO_2 was not explored at this temperature.



Run	0	8	4	6	9	12	14
K_2SO_4 %	-	79	58	78	75	75	-
Na_2SO_4 %	-	21	16	21	20	20	-
NaCl %	-	-	1	1	5	5KCl	100
Misc. %	-	--	25Fe_2O_3	-	-	-	-

FIGURE 25. LABORATORY CORROSION RESULTS AT 800 F

Specimens were exposed to the salt mixtures under a furnace-gas atmosphere for 50 hours.

No attack on Type 321 stainless steel was observed at 800 F, although this material had corroded in some experiments performed at 1000 F. The effects of alkali-metal chloride addition and of the presence of SO_2 in the flue gas at 800 F were similar, in general, to those observed at 1000 F with carbon steels. The corrosive action of KCl and NaCl at the 5 percent level was less at 800 F than at 1000 F.

Corrosion at 600 F

Since the field studies showed that fireside wastage could occur at metal temperatures of 600 F and lower, extensive laboratory studies were carried out with a variety of salt compositions. The standard synthetic flue gas was used, with additions of HCl as noted.

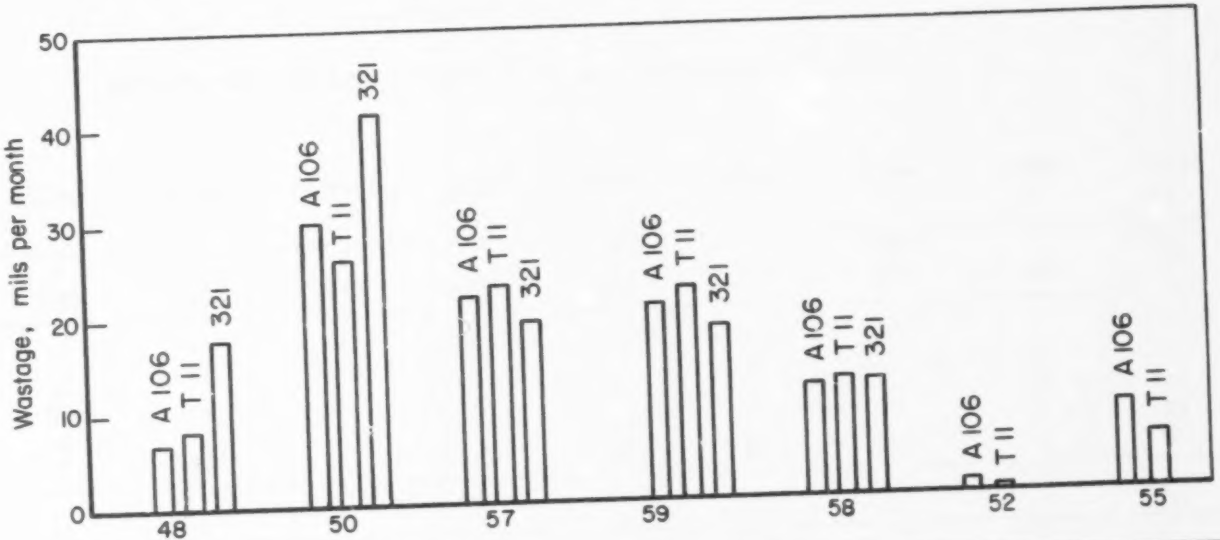
The most corrosive salts examined at 600 F were the bisulfates and pyrosulfates. These were picked because of their low melting points and because they had been demonstrated to be of importance in low-temperature boiler-tube corrosion in fossil-fuel-fired boilers.(43) They were also likely suspects here because the field studies showed that sulfur-bearing salts were involved in the corrosion.

The results with potassium bisulfate mixtures are summarized in the bar graphs in Figure 26. It can be seen in Run 48 that appreciable corrosion occurred in the pure salt and that the stainless steel was more severely attacked than were the carbon steels. The reason for this attack on the stainless steels is not apparent. A base-line comparison of a run without bisulfate can be found in Figure 27, Run 22. The addition of 5 percent NaCl to the bisulfate increased the attack by a factor of 3 or 4 (Run 50). The addition of 5 and 10 percent $ZnCl_2$ along with the NaCl did not increase corrosion (Runs 57 and 58). Similarly, the introduction of 2000 ppm HCl to the flue gas did not accelerate corrosion (Run 59). The addition of $ZnSO_4$ and PbO to the NaCl-bisulfate mixture decreased corrosion (Run 52) and so did the addition of $PbCl_2$ and $ZnCl_2$ (Run 55). It should be pointed out, however, that at 1000 F, $PbCl_2$ and $ZnCl_2$ accelerate corrosion.

It should be noted that all these mixtures were molten during tests and that the corroded metals gave a positive test for sulfide.

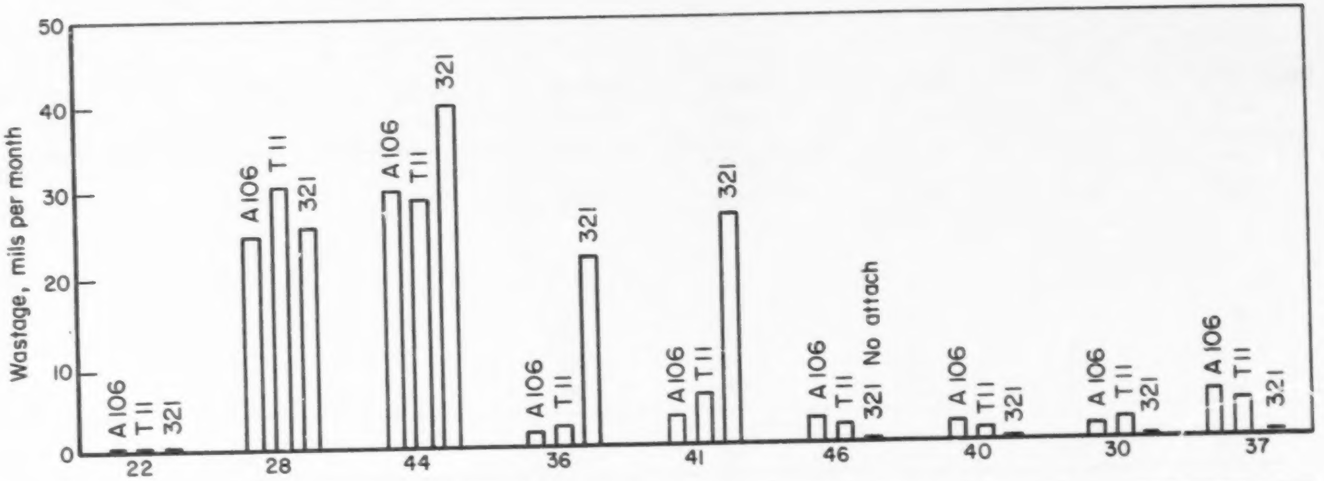
As can be seen in Figure 27, $K_2S_2O_7$ caused greatly accelerated attack on carbon and stainless steels at 600 F (Run 28); however, dilution with inert components greatly reduced the action. The addition of NaCl caused very little increase in the attack (Run 44). The high rate of the attack on stainless steel was maintained when $ZnCl_2$ was added, but the attack on the carbon steels was decreased (Runs 36 and 41). Other additions of oxides, chlorides, and sulfates decreased the corrosiveness of the $K_2S_2O_7$ (Runs 46, 40, 30, and 37). Figure 27 shows that the more corrosive mixtures were those which had been molten during the test.

The mixture of K_2SO_4-Na_2SO_4 and 5 percent NaCl which corroded the steels at 800 and 1000 F did not cause much attack at 600 F in 50 hours, as can be seen in Figure 27 (Run 22).



Run	48	50	57	59	58	52	55
KH SO_4 %	100	95	90	90	80	50	50
NaCl %	—	5	5	5	10	5	5
Zn Cl_2 %	—	—	5	5	10	—	30
Misc %	—	—	—	—	—	30 Zn SO_4	15 Pb Cl_2
Misc %						15 Pb O	—
SO_2 ppm	250	250	250	250	250	250	250
HCl ppm	—	—	—	2000	—	—	—
Azide	+	+++	+++	+++	+++	+++	+++
Physical state	Fused	Fused	Fused	Fused	Fused	Fused	Part fused

FIGURE 26. EFFECT OF KH SO_4 ON CORROSION AT 600 F



Run	22	28	44	36	41	46	40	30	37
$K_2S_2O_7$ %	–	100	25	95	95	65	50	5	5
K_2SO_4 %	75	–	–	–	–	–	–	71	67
Na_2SO_4 %	25	–	–	–	–	–	–	19	19
NaCl %	5	–	5	–	–	5	ZnO, CaO	5	5
Misc %	–	–	–	5 $ZnCl_2$	5 $ZnCl_2$	30 Fe_2O_3	Al_2O_3	–	5 $ZnCl_2$
SO_2 ppm	250	250	250	250	250	250	250	250	250
HCl ppm	–	–	–	–	–	–	2000	–	2000
Azide test	+	+++	+++	+++	+++	+++	+++	+	+++
Physical state	Agglom	Fused	Fused	Fused	Fused	Agglom	Caked	Caked	Caked

FIGURE 27. EFFECT OF $K_2S_2O_7$ ON CORROSION AT 600 F

DISCUSSION OF CORROSION MECHANISMS

The results of studies of the deposits and scale formed on fireside tubes and probes in incinerators combined with the laboratory studies have provided an explanation of the cause of corrosion. Other discussions on the same subject can be found in References 44 through 54. As would be expected, several reactions are coupled and interrelated so that the overall picture is necessarily complex. The following paragraphs outline the processes which are believed to be taking place.

The effects of various constituents are discussed individually; they can act in combination in practice.

Effect of Chlorides and Metal Salts

It is significant that chemical, electron-microprobe, and X-ray analyses show that chlorides are present throughout the deposit and at the scale/metal interface. The fact that $FeCl_2$ has been identified by X-ray analysis in the scale at the interface layer over the entire temperature range studied is considered to be important. It is thought that this iron chloride corrosion product is initially formed from the reaction of iron with the hydrogen chloride or elemental chlorine released at the scale/metal interface.

Hazardous corrosive conditions from deposited chlorides have already been pointed out by Cutler and his associates(53), particularly as they apply to burning fossil fuel containing chlorine.

It is suggested that the corrosive agent hydrogen chloride is released by the reaction:

$$2KCl + SO_2 + 1/2\, O_2 + H_2O \rightarrow K_2SO_4 + 2HCl \quad . \qquad (1)$$

The hydrogen chloride then reacts with the iron surfaces to form ferrous chloride as indicated by:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \quad . \qquad (2)$$

As indicated by the laboratory studies at Battelle and supported by the work of Brown, DeLong, and Auld(55) (see Figure 28), the corrosive effects from HCl would not be expected to be severe below temperatures of about 600 F.

Since $FeCl_2$ has been detected on corrosion-probe samples exposed at temperatures well below 600 F, it is believed that some other mechanism is operating in this temperature range.

Although elemental chlorine has not been identified in incinerator furnace gases and would not be expected at high gas temperatures, it is believed that it may play a role in the corrosion reaction. It is postulated that metal oxides, possibly Fe_2O_3 or PbO, on the tube surfaces catalyze the reaction:

$$2HCl + 1/2\, O_2 \rightarrow H_2O + Cl_2 \quad . \qquad (3)$$

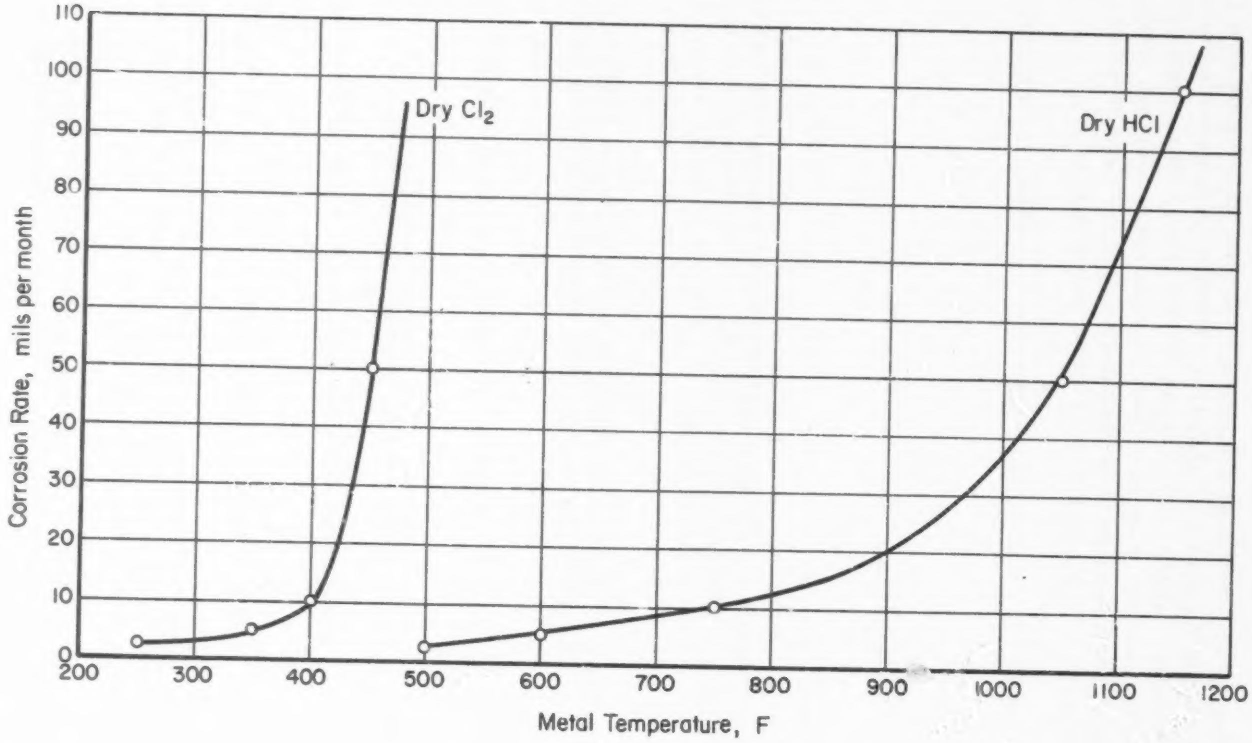


FIGURE 28. CORROSION OF CARBON STEEL IN CHLORINE AND HYDROGEN CHLORIDE(55)

The chlorine, which is formed only near the catalytic surface, then combines directly with the iron by Reaction (4):

$$Fe + Cl_2 \longrightarrow FeCl_2 \quad . \tag{4}$$

It has been shown that once a layer of $FeCl_2$ has formed on the iron surface, reactions forming iron oxides (Fe_2O_3 and Fe_3O_4) and sometimes sulfides take place. Microscopic examination of the scales has shown that a molten salt phase has been present at points within the scale and as an interface layer between the scale and the deposit. This, of course, would act as a barrier to the motion of gases in and out of the layer adjacent to the metal surfaces. Under oxidizing conditions, it would be expected that $FeCl_2$ (and also FeS) would react with oxygen to form Fe_2O_3.(56, 57) Under reducing conditions, on the other hand, it would be expected that this oxide would be reduced to Fe_3O_4. It is suggested that once a thin scale has formed on the metal tubes, such a cycling takes place. The mixed-oxide and molten-salt layers limit the availability of oxygen and retain chlorine and sulfur within the adherent scale.

It has been shown by Fassler(45) that the reaction involved could be:

$$4FeCl_2 + 3O_2 \longrightarrow 2Fe_2O_3 + 4Cl_2 \quad . \tag{5}$$

The chlorine retained within the scale deposit then reacts further with the iron according to Reaction (4).

Three observations suggest that chlorine may be involved. First, as was just mentioned, ferrous chloride is found next to the corroded tube wall even at the low-temperature end of the corrosion probe. Second, the reaction of chlorine with carbon steel is extremely rapid at temperatures of 400 F and higher. The curve in Figure 28 taken from the work referred to earlier(55) shows the high corrosion rate of carbon steel in dry chlorine at low temperatures. Third, the Deacon Process (Reaction 3) is favored at temperatures near 500 to 700 F in the presence of catalysts. Thus it is suggested that chlorine reactions with steel are important at the low temperatures, and that, possibly, HCl and Cl_2 reactions take place at the high temperatures.

The release of Cl_2 and HCl directly adjacent to the tube wall is an important part of the mechanism just proposed. It is of course necessary to explain how the chlorides reach the tube surfaces. It is suggested that the relatively short residence time in an incinerator would favor the deposition of any chloride originally present in the refuse. It has been well demonstrated that solid-phase chlorides can be volatilized during burning processes.(58, 59)

The observation that measurable amounts of chlorides are found in incinerator deposits agrees quite well with the work reported by Bishop(38) on the combustion of coal containing 0.9 percent chlorine. He showed that initial deposits could contain up to almost 40 percent sodium chloride at temperatures near 900 F.

Other chlorides in the deposits come via HCl which is released when chlorinated plastics such as PVC are burned. This HCl then combines with the K_2O and Na_2O which are also refuse combustion products. The reaction is:

$$K_2O + 2HCl \longrightarrow 2KCl + H_2O \quad . \tag{6}$$

It is proposed further that some of the chloride found on the corrosion probes has been transferred as $PbCl_2$ or $ZnCl_2$. According to Sarvetnick(60) compounds such as dibasic lead phosphate, dibasic lead stearate, lead sulfate, lead chlorosilicate, dibasic lead phthalate, zinc 2-ethylhexoate, zinc laurate, and zinc stearate are added to PVC as thermal stabilizers. They act in this capacity because of their ability to react with the HCl liberated from the polymer as it is thermally decomposed. This can account at least in part for the presence of lead and zinc salts on the corrosion probes. Additional lead and zinc compounds of course could come from the volatilization of metal scrap in the refuse. They are probably first released as oxides in the flame and then are converted to sulfates and chlorides on the tubes.

Part of the deleterious function of the lead and zinc salts, particularly chlorides, could be the formation of molten-salt layers, since their melting points are low and since when mixed with other chlorides (NaCl, KCl) they form eutectic compositions which melt at even lower temperatures. These low-melting materials permeate and destroy the initial oxide scale so that the substrate metal becomes exposed to chlorine as it is released from the chlorides in subsequent reaction with furnace gases.

Effect of Sulfur Compounds

It is believed that sulfur-bearing compounds play an important role with regard to corrosion at both low and high temperatures. For example, the most corrosive salts studied in the laboratory at 600 F were the pyrosulfates and the bisulfates. It is suggested that this high corrosivity is related to the fact that these materials have relatively low melting points, i.e., about 575 F for $K_2S_2O_7$ and 415 F for $KHSO_4$. Since the corrosion reactions, which are electrochemical in nature, can take place more readily in liquids than in solids or gases, the presence of a liquid phase is of great importance. It is believed, as was implied earlier, that the melting points of these salts is further modified, possibly lowered, by the zinc and lead salts also shown to be present on the corroded samples.

It is suggested that one of the significant corrosion reactions causing wastage of the metals in incinerators at temperatures near 500 F and higher is the same one proposed many years ago by Corey and his associates(43, 61) and recently by Coates(62) to account for boiler-tube corrosion in fossil-fired furnaces, namely:

$$Fe_2O_3 + 3K_2S_2O_7 \rightarrow 2K_3Fe(SO_4)_3 \ . \qquad (7)$$

It is proposed further that the following reactions also take place to some extent:

$$2KHSO_4 + 3Fe \rightarrow Fe_2O_3 + FeS + K_2SO_4 + H_2O \qquad (8)$$

$$K_2S_2O_7 + 3Fe \rightarrow Fe_2O_3 + FeS + K_2SO_4 \ . \qquad (9)$$

In addition to the laboratory evidence showing the corrosivity of these materials, it should be pointed out that the azide and pH tests made on the individual corrosion-probe specimens show the presence of sulfide and the presence of acidic hydrolyzing salts on the majority of the specimens. The presence of sulfide helps validate Reactions (8) and (9) above.

Sulfur was also detected with the microprobe at areas near the metal surface.

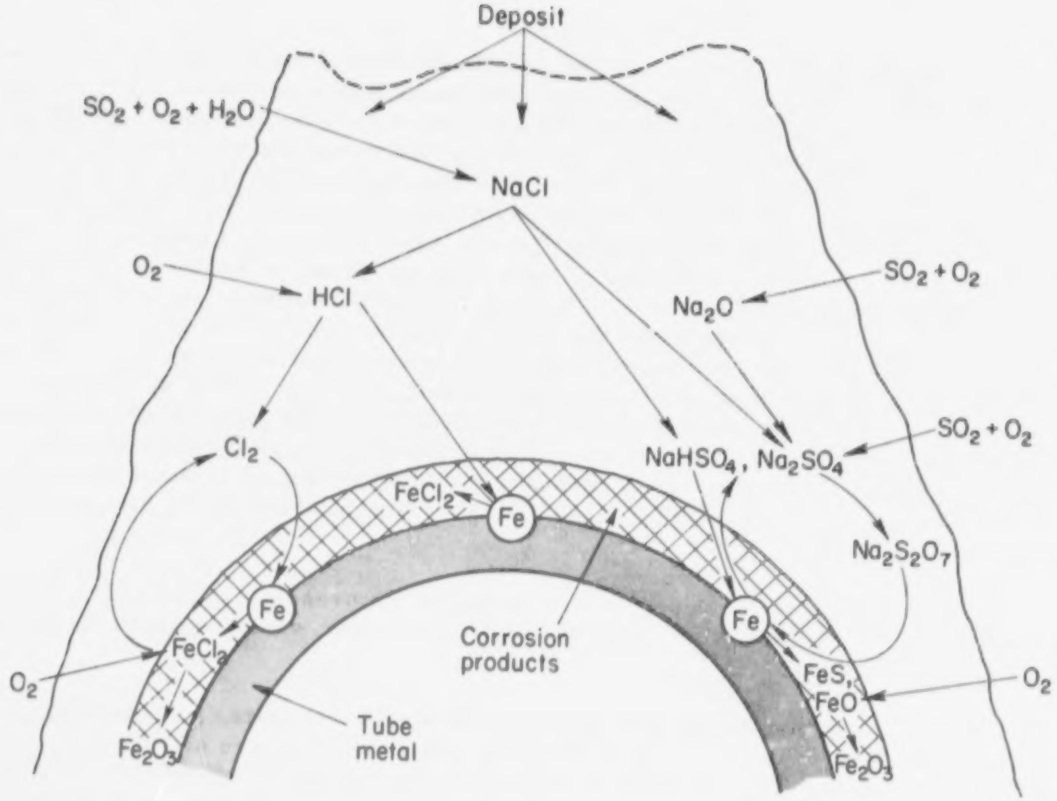
The fact that sulfide is formed in the corrosion scale suggests that the oxygen pressures beneath the scale must be very low, probably of the order of 10^{-14} atmosphere. This is indicated because it has been shown(57) that a sulfur pressure of 10^{-13} atmosphere is sufficient to produce FeS when SO_2 and O_2 pressures are below 10^{-14} atmospheres. At higher SO_2 or O_2 pressures, iron oxides form. When oxides are present on the iron surface, higher sulfur pressures and perhaps moisture(63) are needed to form FeS.

The dimpled surface structure of the specimens mentioned earlier is related to the presence of both FeS and $FeCl_2$ phases at the metal/scale interface. It is suggested that the reason for the dimpling is the variation in the corrosion through these phases which coat adjacent areas on the tubes. Because of the cation vacancies in the FeS structure, there is a higher diffusion rate of iron ions through the FeS film than through the $FeCl_2$ film, which is more ionic in character, has fewer cation vacancies, and thus a lower cation diffusion rate. The driving force for this diffusion in both cases is the iron concentration gradient established by the formation of the more stable iron oxides at the exterior surface of these films. The oxide formation depends upon the SO_2 or O_2 penetrating the mixed-oxide scale and the other deposits. The presence of $FeCl_2$ or FeS at the metal/scale interface suggests that the environment at the metal surface is sufficiently low in oxygen pressure to prevent formation of iron oxides which have 10 to 20 percent larger free energy of formation than either the chloride or sulfide over the temperature range of interest. However, the chloride and sulfide are slowly oxidized to Fe_2O_3 at the surface away from the metal substrate so that the chlorine or sulfur in the respective phase is increased and the reaction proceeds by attack of the substrate metal.

The low pH of the waste deposits also suggests the presence of the acid sulfates or pyrosulfates. Of course, zinc chloride and iron chloride would also give an acidic reaction upon hydrolysis.

The presence of bisulfates, pyrosulfates, or alkali trisulfates has not been proved by X-ray diffraction. This, of course, does not mean that they are not present, since previous studies at Battelle and elsewhere have shown that these materials are difficult to detect in small amounts. Dilution of these phases with normal sulfates reduces the attack on the steels by very significant amounts.

The sequence of the chemical reactions discussed in the preceding paragraphs has been summarized in Figure 29, which illustrates the proposed corrosion mechanism.



Deposit
$SO_2 + O_2 + H_2O$
NaCl
O_2
HCl
$SO_2 + O_2$
Na_2O
Cl_2
$NaHSO_4$, Na_2SO_4
$SO_2 + O_2$
$FeCl_2$
Fe
$Na_2S_2O_7$
Fe
Fe
Corrosion products
$FeCl_2$
O_2
FeS,
FeO
O_2
Fe_2O_3
Tube metal
Fe_2O_3

FIGURE 29. SEQUENCE OF CHEMICAL REACTIONS EXPLAINING CORROSION ON INCINERATOR BOILER TUBE

CONCLUSIONS

General

These field and laboratory studies have demonstrated that the wastage in waterwall refuse boilers can be more severe than that normally encountered in fossil-fuel-fired boilers. The complex nature of the refuse used as the fuel and the relatively poorer control of burning in an incinerator combine to increase the possibility for corrosion. The contributors to the attack are corrosive gases and low-melting chloride and sulfur-containing salts which exert a fluxing action on the protective films on the metal surface. These low-melting salts primarily contain compounds such as zinc and lead chlorides along with potassium bisulfate and potassium pyrosulfate. The data developed reveal that the gases SO_2, SO_3, HCl, and Cl_2 are also playing a major role in the wastage processes.

Analyses of tube deposits and furnace gases confirm the belief that sufficient quantities of the deleterious salts and gases are present in all municipal incinerators to warrant careful consideration from a corrosion standpoint.

Tube Wastage

The work carried out with the corrosion probes inserted in the incinerators has demonstrated that the wastage rates of boiler-tube metals are directly related to the operating metal temperatures. Some attack will be experienced in the 300 to 600 F range and greatly increased rates can be anticipated as temperatures are raised to 1000 F. The temperature gradient between the metal surface and the furnace atmosphere is also important. Thus, relatively low metal temperatures are to be preferred in flame areas.

The corrosion rates shown on the bar graphs in earlier sections of this report should not be used to project wastage values to be expected after long exposure periods such as a year or more. This is because the initial rates are always high and the rates decrease appreciably as the exposure time increases. The protective action of the tightly adhering scale probably accounts for this decrease in attack. Thus, rates for carbon steel tubes at about 500 F might be expected to range below about 10 mils per year for extended exposure periods rather than the much higher rates calculated using the bar-graph data. However, scale removal to improve heat transfer could adversely affect the corrosion behavior.

While the stainless steels, particularly Types 310 and 446, furnish good resistance to fireside corrosion, their use is limited because of the deleterious effects which can take place during downtime under humid conditions. The Type 310 can fail because of stress-corrosion cracking and the Type 446 can be severely pitted. However, only minor pitting occurred in incinerator operation. The other austenitic stainless steels evaluated – Types 304, 316, and 321 – also were more resistant than the carbon steels but are subject to SCC. The Type 416 stainless steel did not perform well enough to be seriously considered. The Inconel 600 and 601 materials were quite resistant over the lower temperature region 300 to 500 F but were severely attacked at higher temperatures and thus are not good choices.

Incoloy 825 gave encouraging results over the entire temperature range and is much more resistant to SCC than the austenitic stainless steels so it could be considered for use in high-temperature areas where the carbon steels would not be recommended.

While the aluminum, chromium, and inorganic coatings furnished some initial protection to the tube surfaces they do not appear to be sufficiently durable to be considered for long-time boiler operation.

Incinerator Operation

Several criteria of boiler operation can be suggested from the research results which should increase incinerator boiler life and reduce maintenance costs.

(1) It is concluded that water-wall incinerators should not be used to generate high-temperature superheated steam, but should be operated at relatively low metal temperatures, near 500 F, to minimize tube wastage. If high-temperature superheated steam is desired for more efficient power production, it appears that there is merit in using the refuse to heat the water in a separate furnace and do the additional heating in another furnace with fossil fuel as the heat source. Thus corrosive deposits and gases will be kept away from tubes operating at high metal temperatures.

It is of interest in this connection to compare the nominal operating conditions of some of the water-wall installations on this continent with those in Europe and England. Given in Table 9 are steam temperatures and pressures and the nominal tube-metal temperature, arbitrarily chosen to be 50 degrees above the steam temperature, for several stations operating and several being constructed. It can be noted that the European practice, except for those at Rotterdam and Coventry, is to operate at relatively high temperatures and pressures. Severe metal wastage has been reported for some of these stations. On the other hand, the units at Norfolk have not shown corrosion. It is believed that the excellent performance of the Norfolk installation to date is related to the fact that the operating pressure there has been kept very low, i. e., 175 to 200 psi. Allowing for a 50 F rise through the metal wall, this corresponds to a metal surface temperature of about 425 to 440 F. Since the cool water flows to the bottom of the wall tubes and then rises, the metal temperatures in the flame area are probably even lower than 425 F.

It is interesting to note that the trend in design of new water-wall incinerators on this continent has been in the direction of operation at moderate boiler tube temperatures.

(2) It is concluded that downtime could be a critical corrosion period for a refuse boiler in that hygroscopic salts on the tubes could become wet and cause attack. Such attack, however, has not occurred at Norfolk where the two boilers are operated alternately every other week. Nevertheless, it is believed that maintaining warm, dry tubes at all times is worthwhile. As a corollary it would appear that operation of the units 7 days a week, 24 hours a day would be optimum. Furthermore, metal temperatures in the boiler and in the effluent gas stream should be kept high enough to avoid either H_2SO_4 condensation or HCl/H_2O dewpoint condensation. Staying above about 300 F should prevent the former and above 225 F for the latter.

TABLE 9. NOMINAL OPERATING CONDITIONS OF WATER-WALL INCINERATORS

Location	Steam Pressure, psig	Steam Temp, F	Metal Temp, F (Approx.)
Milan, Italy	500	840	890
Mannheim, Germany	1800	980	1030
Frankfurt, Germany	960	930	980
Munster, Germany	1100	980	1030
Moulineaux, France	930	770	820
Essen Karnap, Germany	--	930	980
Stuttgart, Germany	1100	980	1030
Munich, Germany	2650	1000	1050
Rotterdam, Netherlands	400	680	730
Edmonton, England	625	850	900
Coventry, England	275	415	465
Amsterdam, Netherlands	600	770	820
Montreal, Canada	225	395	445
Chicago (N.W.), Illinois	265	410	460
Oceanside, New York	460	465	515
Norfolk, Virginia	175	375	425
Braintree, Massachusetts	265	410	460
Harrisburg, Pennsylvania	275	460	510
Hamilton, Ontario	250	400	450

(3) Although not examined in the current program, the European practice of attempting to avoid all operation where reducing conditions can occur has much merit. In this connection the control of the burning and the feeding of the refuse can be of great importance. It should be pointed out that many years of research were required to develop the best techniques for burning the fossil fuels coal and oil with a minimum of corrosion. Fuel preparation and burning control are an important part of that technology. Similarly, if refuse is to be considered a fuel it should be treated as such and not fired as it comes from the pickup trucks.

INCINERATOR WET SCRUBBER CORROSION

(Research Grant EP-00325-03S1)

During Year 3 of the grant program, a supplemental study was conducted on corrosion problems associated with wet scrubbers used with municipal incinerators. This grew out of the observation that scrubber corrosion was as serous or even more so than fireside corrosion. Two areas of study were pursued on this phase of the program. First, a survey of the current corrosion status of many operating scrubbers throughout the eastern United States was conducted by means of plant visits and correspondence or by telephone. Second, an on-site corrosion study was conducted in the scrubber at the North Montgomery County Incinerator, near Dayton, Ohio.

Corrosion Status Survey

The nature and extent of incinerator scrubber corrosion was discussed with the operating personnel during visits to the following municipal incinerators:

Crookshank, Cincinnati, Ohio
East Hartford, Connecticut
East 73rd Street, New York City
Framingham, Massachusetts
Greenpoint, Brooklyn, New York
Montgomery County, North, Dayton, Ohio
Montgomery County, South, Dayton, Ohio
Miami County, Troy, Ohio
Waterbury, Connecticut.

Correspondence or verbal communication on incinerator operation and scrubber corrosion has also been received from the following:

Almeida, Richard, Ft. Lauderdale, Florida
Axtell, Wm. R., Ethyl Corporation, Louisiana
Hall, P. B., City of Alexandria, Virginia
Hilsheimer, H., Mannheim, Germany
Hollander, Herbert I., Roy F. Weston, Engineers, Pennsylvania
Nowak, Frank, Stuttgart, Germany
Odle, James, Homes Road Incinerator, Houston, Texas
Sebastian, F. P., Envirotech Corporation, California
Tuckett, Norman, Ft. Lauderdale, Florida
Velzy, Charles, O., Charles R. Velzy Associates, New York
Whitewell, Joseph A., Chemical Construction Corporation.

Useful information on incinerator corrosion was also obtained from:

The International Nickel Company
Engineering Foundation Research Conference, August 23-27, 1971,
Deerfield, Massachusetts

Solid Waste Management Office, Incinerator
Corrosion Conference, April 12, 1971
ASME Incinerator Division meetings.

The assistance furnished by all of the above individuals and organizations is gratefully acknowledged.

There is general agreement that the corrosion in wet scrubbers for incinerators is an extremely severe problem. The rapid attack of most metals and alloys is not too unexpected when the composition and complexity of the effluent gases and dusts coming from the burning chamber are considered. These gases include corrosive constituents such as HCl, SO_2, SO_3, HF, and organic acids. A detailed discussion of the gaseous by products from an incinerator are found in earlier sections of this report along with measurements of the composition of the dusts carried by the gases. Extensive measurements of incinerator effluent gases have been reported by Carrotti and associates during the past few years.(64, 65, 66) One of their earlier measurements at the East 73rd Street Incinerator in New York City indicated an HCl evolution of up to 8 lb/ton of refuse. This incinerator did not use a scrubber but did contain water-spray chambers. Thus, some of the HCl was probably removed ahead of the stack where the measurements were made. Since well-designed scrubbers will remove much more of the soluble gases, it would follow that a relatively small incinerator of say 200 T/day could be absorbing up to 1600 lb/day of HCl in the scrubber water. Large amounts of sulfur-containing acids would also be absorbed.

The presence and concentration of HCl is of particular concern because this material accelerates pitting of most construction materials. It also limits the use of austenitic stainless steels because of the possibility of stress-corrosion cracking. The importance of HCl in causing severe corrosion of equipment has been well documented. Hanna and Curley, for example, showed that even trace amounts were damaging.(67) Kear reported increased corrosion from HCl in combustion gases.(68) Piper and VanVliet some time ago pointed out that accelerated corrosion results from HCl as the water dewpoint was reached in a power station burning coal.(69)

There are many possible sources of HCl in an incinerator. Some, but not all, of this gas comes from burning plastics. The subject of combustion products including HCl from burning plastics has been widely discussed, as in References 70 to 79.

It has been found at many locations that the pH of the scrubber water soon drops to a low value, i.e., about 2.0. This is particularly true if the water is recirculated as is the practice in many places.(80, 81, 82) An example of such an operation is at Montgomery County, Ohio. Data furnished by that office have been tabulated in Figure 30, which shows the buildup of various constituents in the scrubber water at the South Plant over about a 2-week period. It can be seen that the pH remained quite low near 2.5 and that the chloride rose from about 9,000 ppm to 40,000 ppm. The sulfate, on the other hand, remained near 2,000 to 3,000 ppm and then abruptly rose to 25,000 ppm. Other dissolved solids, conductivity, etc., also rose as the operation continued. Thus, with all these acidic components present, it is easy to see why the corrosion is so severe in these systems. It is estimated that the buildup of chloride in the circulating solution in the example cited above amounted to about 500 lb/day.

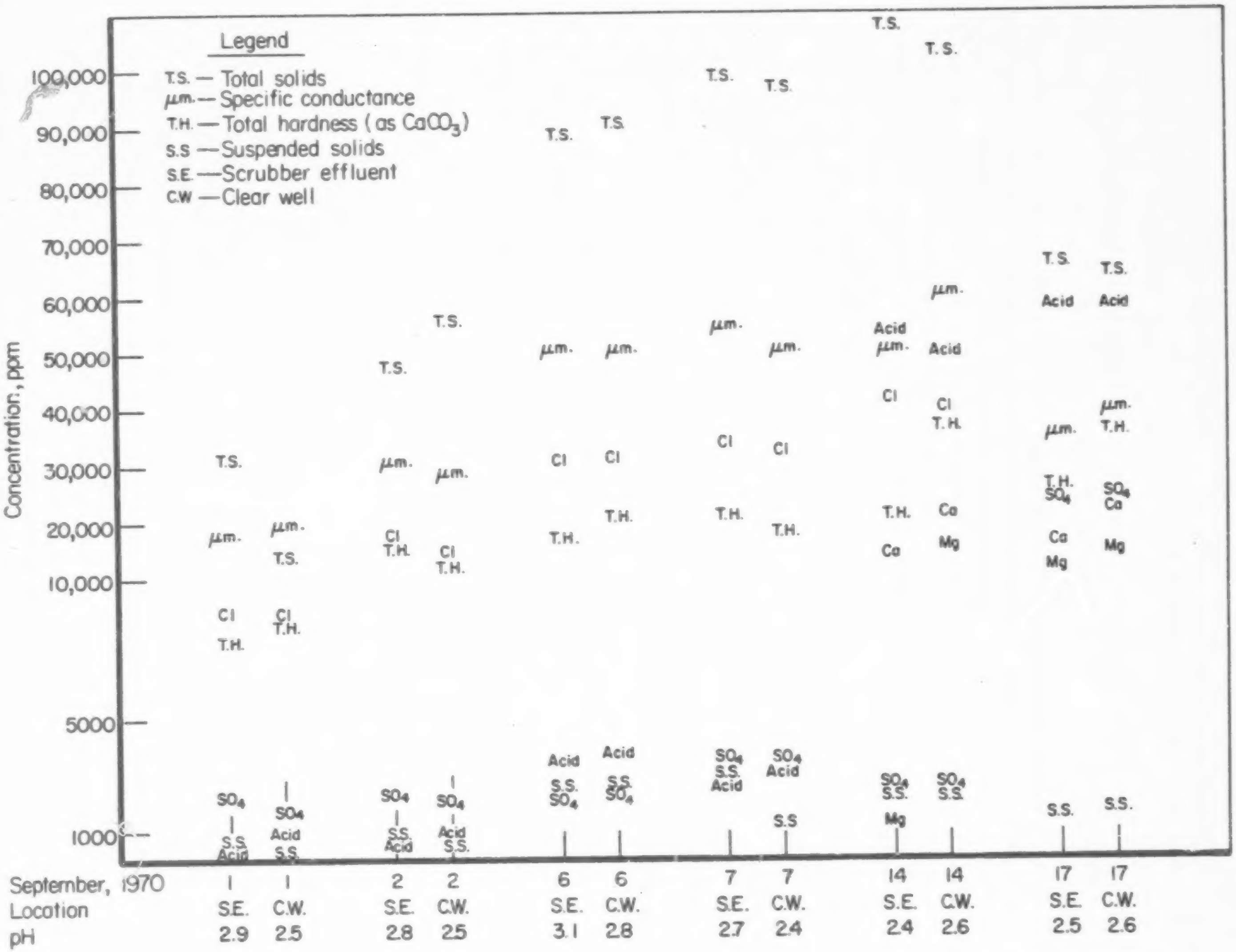


FIGURE 30. CHANGE IN COMPOSITION OF SCRUBBER WATER DURING CONTINUOUS RECIRCULATION

These data were obtained at the South Montgomery County Incinerator

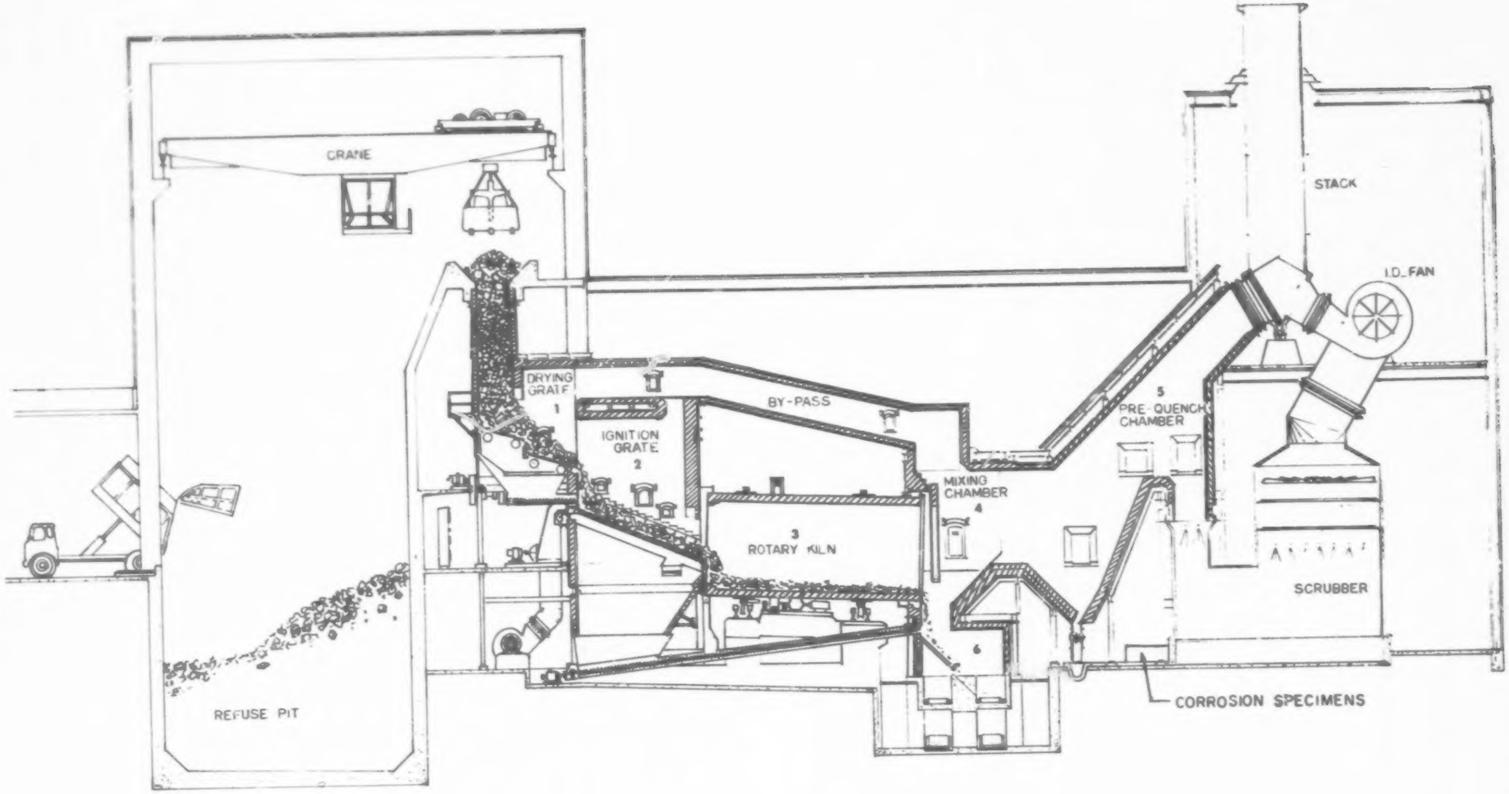

CRANE
REFUSE PIT
DRYING GRATE 1
IGNITION GRATE 2
BY-PASS
3 ROTARY KILN
MIXING CHAMBER 4
5 PRE-QUENCH CHAMBER
6
STACK
I.D. FAN
SCRUBBER
CORROSION SPECIMENS

FIGURE 31. SECTION THROUGH MONTGOMERY COUNTY INCINERATOR PLANTS

The corrosion specimens were submerged in the water in the weir leading from the bottom of the scrubber.

Other factors leading to high corrosion in incinerator scrubber are

(1) Elevated temperatures (140-190 F)

(2) Abundant oxygen supply

(3) High velocities.

The survey showed that a valuable accumulation of corrosion data is available. In summary, there is general agreement that

(1) Carbon steels, cast iron, brass and bronze, are rapidly corroded.

(2) Performance of stainless steels has been variable, ranging from little corrosion to severe wastage and pitting.

(3) The more resistant alloys are Hastelloy C, titanium, and Inconel 625. However, they are quite expensive.

(4) Rubber and plastic coatings have shown some encouraging results, particularly in piping application.

(5) Fiberglas-reinforced plastic pipe and structural components show good resistance to the corrosive solutions as does acid-brick construction.

(6) Both deposits and corrosion can be a problem on induced-draft fans.

(7) Corrosion can be a problem on stacks.

(8) All components and areas in the scrubber are susceptible to corrosion, with the mist eliminator area being the most susceptible to attack.

(9) Concrete supports and flumes can be severely corroded by the hot acid solutions.

Scrubber Corrosion Studies

Procedures

As summarized in the preceding sections a considerable background of corrosion data for incinerator scrubbers is available. The search for this information, however, revealed that no systematic study of stress-corrosion cracking had been conducted in scrubber environments. Some plant failures, of course, had been traced to stress-corrosion cracking. In order to gain a better understanding of corrosion and stress-corrosion cracking in scrubber systems, a fairly extensive exposure program was carried out in the North Montgomery County Incinerator. The specimens were immersed in the hot water (170-190 F) passing through the concrete flume at the base of the scrubbers. The racks holding the specimens were alternated between Units 1 and 2 as the incinerator operation schedule dictated. Figure 31 shows the location of the specimens on a section drawing of the plant. The pH of this scrubber water varied from 4.0 – 5.1 as shown in Table 10, along with compositional data on the effluent water. A duplicate set of specimens was also exposed in the same water at Columbus, Ohio, under static, aerated, conditions at pH 2.0-2.5 to determine the effect of lower pH. The following tabulation lists the eighteen metals and alloys evaluated in these scrubbers. The compositions of the alloys can be found in Table 1. Most were chosen because of their good corrosion resistance and resistance to stress-corrosion cracking, although a few stainless steel composition were included for comparison purposes. The specimen configuration used is illustrated in Figure 32. The specimens to the left are stressed C-rings cut from pipe, those in the center are 4 x 4-inch flat plates containing 2-inch diameter circular welds, and those to the right are U-bends cut from sheet stock. The welded pieces provide an indication of weld durability as well as the effect of stress.

Materials Evaluated in Scrubber

Stainless Steel
304
310
316 L
446

Inconel
600
601
625

Incoloy
825

Armco
22-13-5

USS
18-18-2

Hastelloy
C
C-276
F
G

Carpenter
20 S

Type S-816

Titanium
75 A
6Al-4V

The C-rings and U-bends were mounted in pairs with centers touching as shown. This arrangement provided some indication of the importance of crevice areas. The specimens were held between Teflon strips as illustrated in Figure 33. The C-rings and U-bends were stressed with Type 304 stainless steel bolts. The welded plates were supported on Teflon rods with Teflon spacers. These spacer areas provided additional crevice areas.

A third set of stressed specimens of selected alloys was exposed at Columbus, Ohio, in contact with deposit removed from the ID fans and housing and maintained under hot, humid conditions above scrubber water.

Results From North Montgomery County

The specimens exposed in the scrubber water at North Montgomery County were examined after 8, 17, 38, 63, 96, and 129 days. These specimens rapidly became coated with a very adherent deposit which could be removed only by vigorous scrubbing

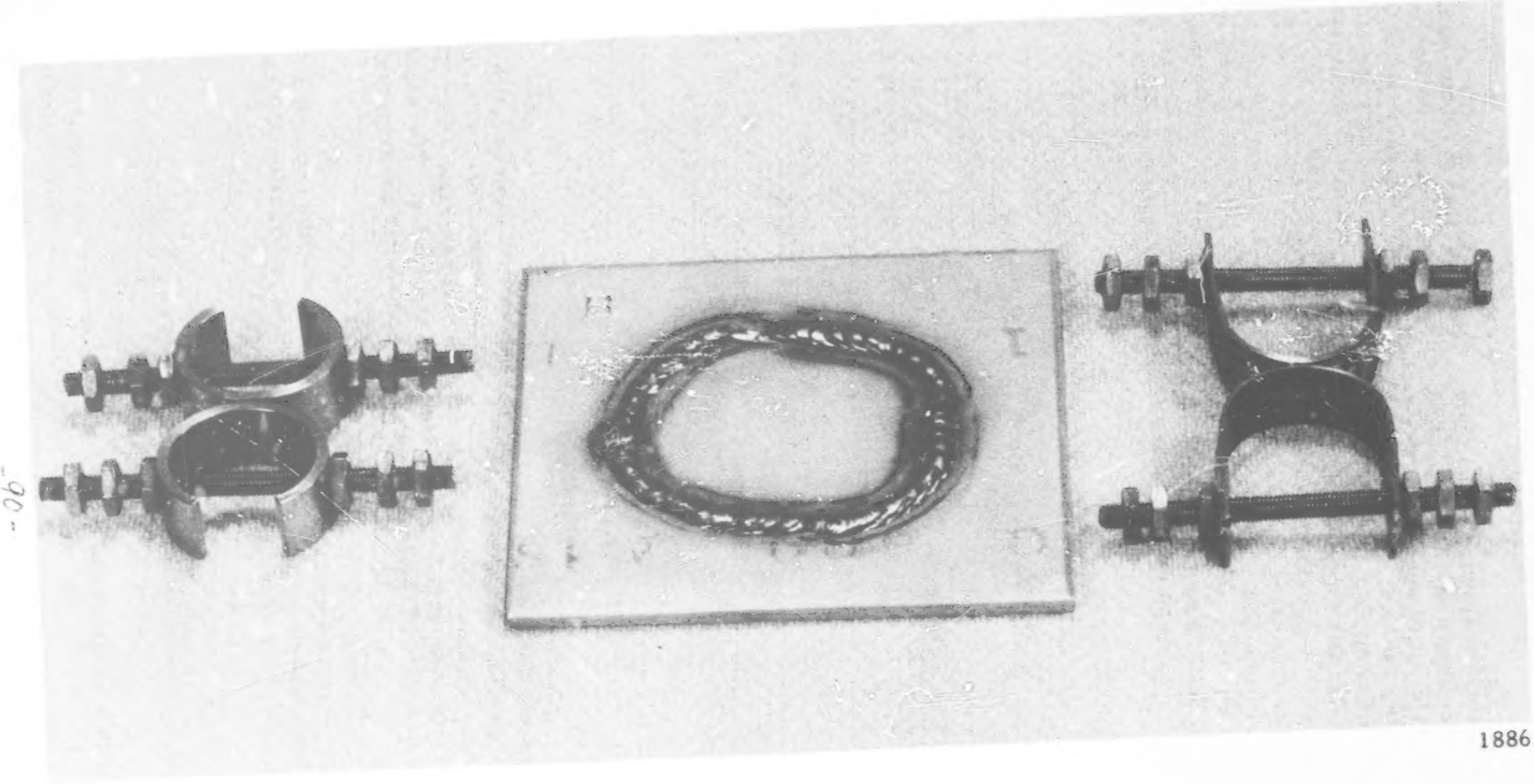
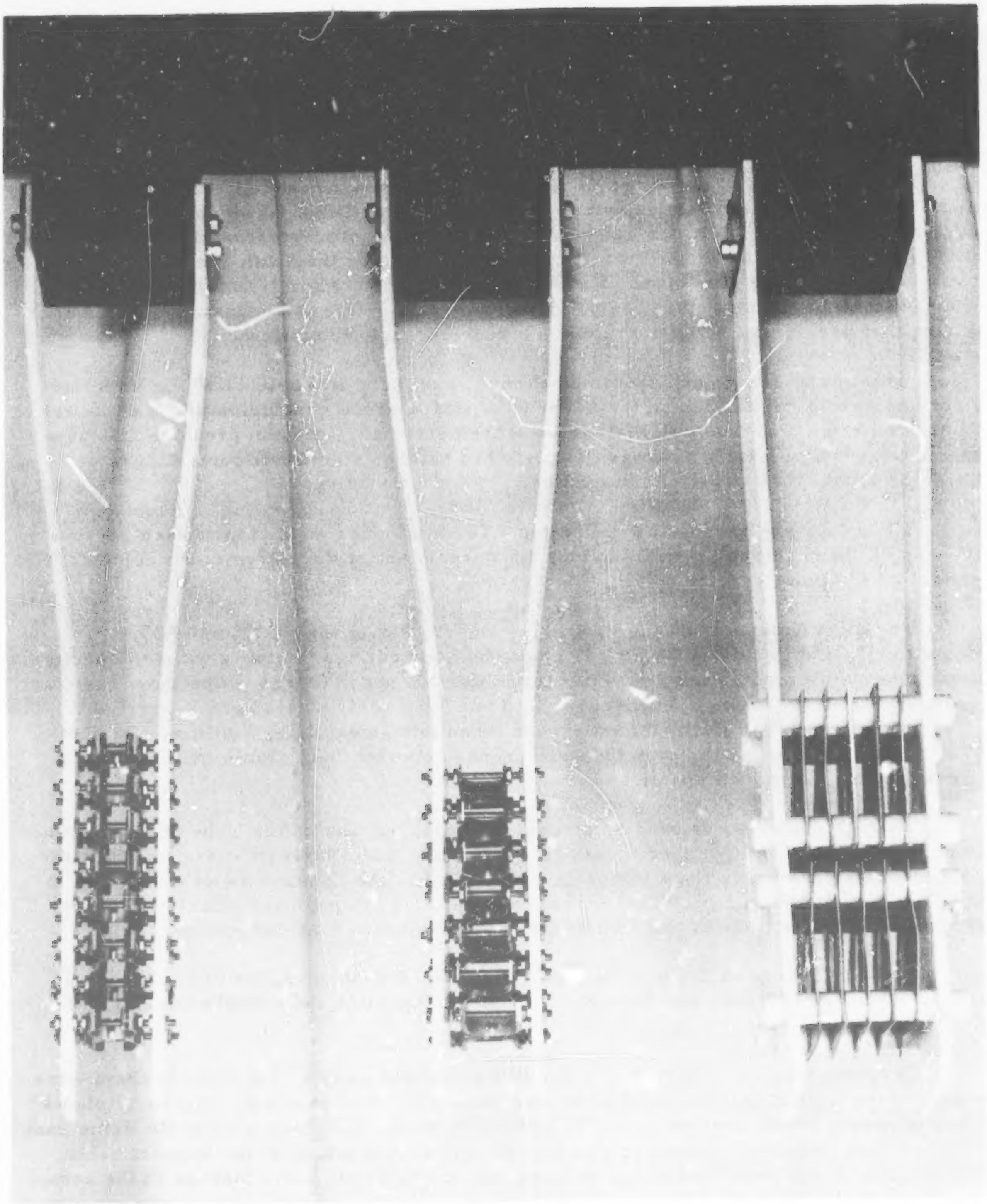


FIGURE 32. TYPES OF SPECIMENS USED TO STUDY CORROSION AND STRESS CORROSION IN INCINERATOR SCRUBBER WATERS



1885

FIGURE 33. MOUNTED SPECIMENS USED IN SCRUBBER STUDY

with a bronze-wire brush. This coating very likely afforded some corrosion protection to the specimens. Spectrographic analyses of the coating showed a major amount of calcium and appreciable amounts of lead, barium, silicon, and aluminum. The low solubilities of calcium, barium, and lead sulfates is consistent with the presence of these deposits. X-ray diffraction studies confirm the presence of $PbSO_4$ and $CaSO_4 \cdot 2H_2O$.

A large portion of the water in this scrubber was recirculated, but a sizeable make up was required. This is evident from the data in Table 10 which includes analyses over a 4-month period. It can be seen that the chloride concentrations never exceeded 2400 ppm, which is ten times lower than was reported for the South Plant where complete recirculation is employed. Furthermore, the results for 12/8/71 in Table 10 show extremely low concentrations of dissolved salts. This is because the scrubber during that period was being operated on a once-through water flow.

Details regarding each specimen exposed are found in Table 11 which lists the first instance of corrosion and the severity of attack at the conclusion of the exposure. Corrosion rates based on weight-loss measurements have not been presented because the attack when present was always localized in nature, so overall corrosion rates based on weight loss would be misleading.

The alloys are arranged with the most resistant ones at the top of each section (C-ring, U-bend, circular weld) and the least resistant at the bottom. Pit depths are shown for the plate specimens.

The most durable materials were Ti-6Al-4V, Hastelloy C, Inconel 625, Hastelloy G, and Hastelloy C-276, as shown by good ratings, in two groups of specimens. Some other alloys were rated good in one section but not in others. The least resistant were Type 304, 304 sensitized, Armco 22-13-5, USS 18-18-2, 445 and Inconel 600. The other materials were intermediate between these extremes. The unalloyed titanium (Ti 75A) was quite resistant and the weld cracks reported in the table may have been present in the as-welded specimens.

The only definite cracking as a result of exposure was on the Type 304, 304 sensitized, and the Inconel 600 specimens. Figures 34 and 35 illustrate these effects after 63 days of exposure. In many respects the attack has the appearance of stress-accelerated corrosion rather than stress-corrosion cracking, particularly for the Inconel. Later sections of this report illustrate typical stress-corrosion cracks.

The appearance of the less durable C-rings and U-bends (Type 304, 304 sensitized, 446, USS 18-18-2, and Inconel 600) after 129 days in the scrubber are shown in Figure 36.

Cracking was not observed in the circular welded panels, but many of them were pitted, often predominantly in the area near the weld. For example, Figure 37 shows a fairly deeply pitted area on Type 316L near the weld. The back side of the same panel after 63 days contained strings of pits as well as crevice attack at the support holes. The strings of pits may be similar to those which finally produced leakage in the actual scrubber wall.

Similar selective attack at the support hole crevices and the pits in the weld area on the back of the Type 310 stainless steel panel were evident.

TABLE 10. SCRUBBER WATER COMPOSITION DURING EXPOSURE PERIOD

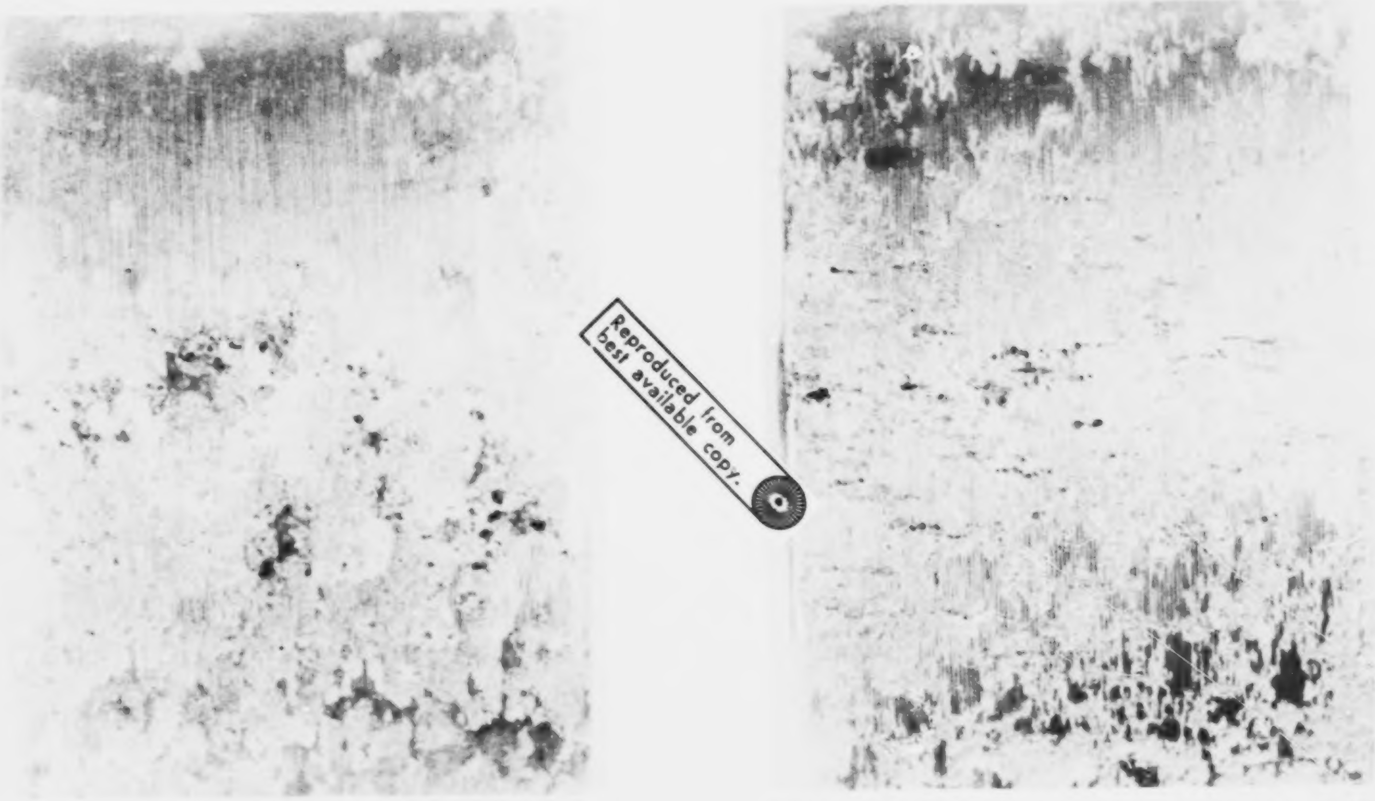
Measurement	Date			
	8/31/71	10/8/71	11/2/71	12/8/71[a]
Total hardness as $CaCO_3$, ppm	2330	2760	6250	272
Calcium as Ca, ppm	568	784	1704	71
Magnesium as Mg, ppm	262	230	573	27
Sulfate as SO_4, ppm	1261	1308	1933	231
Chloride as Cl, ppm	2355	2355	1610	183
Specific conductance μmho/cm	7499	7639	11,160	833
Total solids, ppm	5916	5900	11,386	732
Suspended solids, ppm	114	14	10	114
Total acidity as $CaCO_3$, ppm	402	388	352	68
pH	4-4	4-3	5-1	4-0

(a) On this date the scrubber water was not being recirculated.

TABLE 11. CORROSION RESULTS OF STRESSED AND WELDED SPECIMENS EXPOSED TO SCRUBBER SOLUTIONS AT NORTH MONTGOMERY COUNTY, OHIO[(a)]

Specimen		Corrosion Results	Depth of Attack, mils	
Alloy	Number		Pit	Crevice
		U-Bends		
Ti-6Al-4V	J1	Good resistance 129 days		
	J2	Good resistance 129 days		
Hast C	D1	Good resistance 129 days		
	D	Good resistance 129 days		
625	N1	Good resistance 129 days		
	N2	Good resistance 129 days		
Hast G (welded)	S1	Good resistance 66 days		
	S2	Good resistance 66 days		
Hast C276 (welded)	R1	Good resistance 66 days		
	R2	Good resistance 66 days		
316 L	H1	Good resistance, one pit 129 days		
	H2	Good resistance 129 days		
Carp 20	C1	Very fine pits 63 days, same at 129 days, good resistance		
	C2	Very fine pits 63 days, same at 129 days, good resistance		
Hast F	E1	Very fine pitting 63 days, slight edge attack 129 days		
	E2	Good resistance 129 days		
Armco 22-13-5	T1	Good resistance 33 days		
	T2	Good resistance 33 days		
T75A	K1	Weld-grains etched, possible cracks in weld, 129 days		
	K2	Weld-grains etched, possible cracks in weld, 129 days		
S816	F1	Slight roughening 63 days, same at 129 days		
	F2	Slight roughening 63 days, same at 129 days		
USS 18-18-2	U1	Bad edge and end-grain attack at 33 days		
	U2	Bad edge and end-grain attack at 33 days		
		C-Rings		
825	A1	Good resistance 129 days		
	A2	Good resistance 129 days		
601	M1	Good resistance, slight corrosion at machining lines 129 days		
	M2	Good resistance, slight corrosion at machining lines 129 days		
310	1G	One pit near crevice 63 days, slight pitting near crevice 129 days		
	1H	Slight pitting near crevice 63 days, same at 129 days		
316 L	H1	Some edge attack 63 days, worm track and edge attack 129 days		
	H2	Edge attack 63 days, same at 129 days		
304	3G	Pitting 17 days, rows of pits across face 63 days, possible cracks 129 days		
	3H	Pits 8 days, rows pits across face 63 days, possible cracks 129 days		
304 S	2G	Pitting 38 days, rows pits across face 63 days, possible cracks 129 days		
	2H	Pitting 38 days, rows pits across face 63 days, possible cracks 129 days		
600	B1	Pitting 17 days, deep grooves 63 days, same at 129 days		
	B2	Edge attack 8 days, deep grooves 63 days, same at 129 days		
446	4G	Pitting 17 days, severely corroded, one penetration 129 days		
	4H	Pitting 8 days, severely corroded, deep edge canyons 129 days		
		Circular Welded Plates		
Ti-6Al-4V	J	Good resistance, grains outlined 129 days	0	0
625	N	Good resistance 129 days	0	0
Hast C	D	Good resistance 129 days	0	0
Hast F	E	Good resistance 129 days	0	0
S816	F	Good resistance 129 days	0	0
Carp 20	C	Some crevice attack 129 days	0	4
825	A	Some crevice attack 129 days	0	5
Armco 22-13-5	T	Pitting and crevice attack 33 days	2	15
316 L	H	Pitting and crevice attack 63 days, worse at 129 days	8	20
310	I	Pitting 38 days, deep pits and crevice attack at 129 days	14	32
600	B	Shallow pits 8 days, bad attack surface, weld, edge, crevice at 129 days	30	28
304	G	Pitting 8 days, deep pits, more at heat-affected zone 129 days	20	31

(a) pH 3.0-5.1.
Temperature 170-180 F.
Most specimens examined at 8, 17, 38, 63, 96, and 129 days.



a. Sensitized Specimen 2G

b. Mill-Annealed Specimen 3G

FIGURE 34. APPEARANCE OF TYPE 304 STAINLESS STEEL STRESSED SPECIMENS AFTER EXPOSURE OF 63 DAYS IN INCINERATOR SCRUBBER EFFLUENT

This cracking is not typical of SCC.

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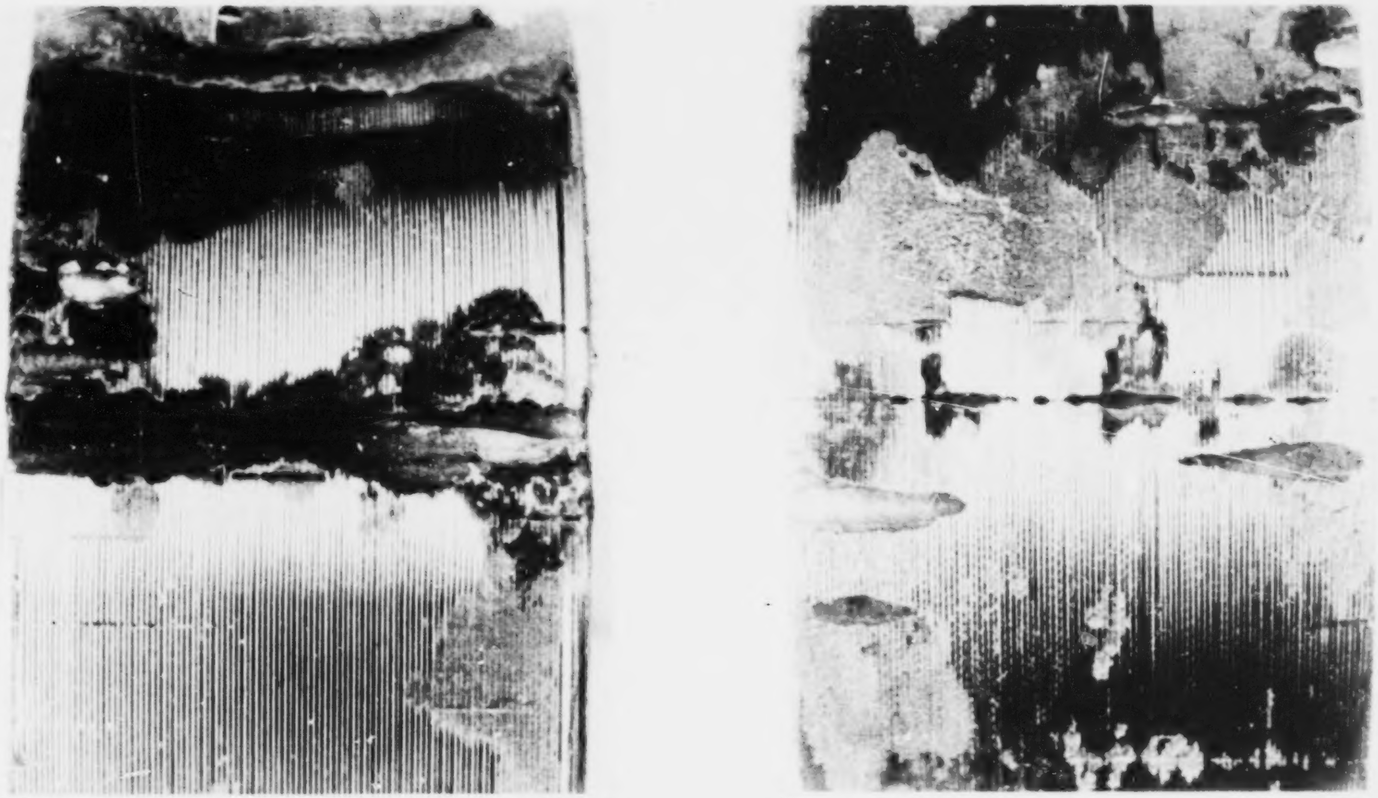
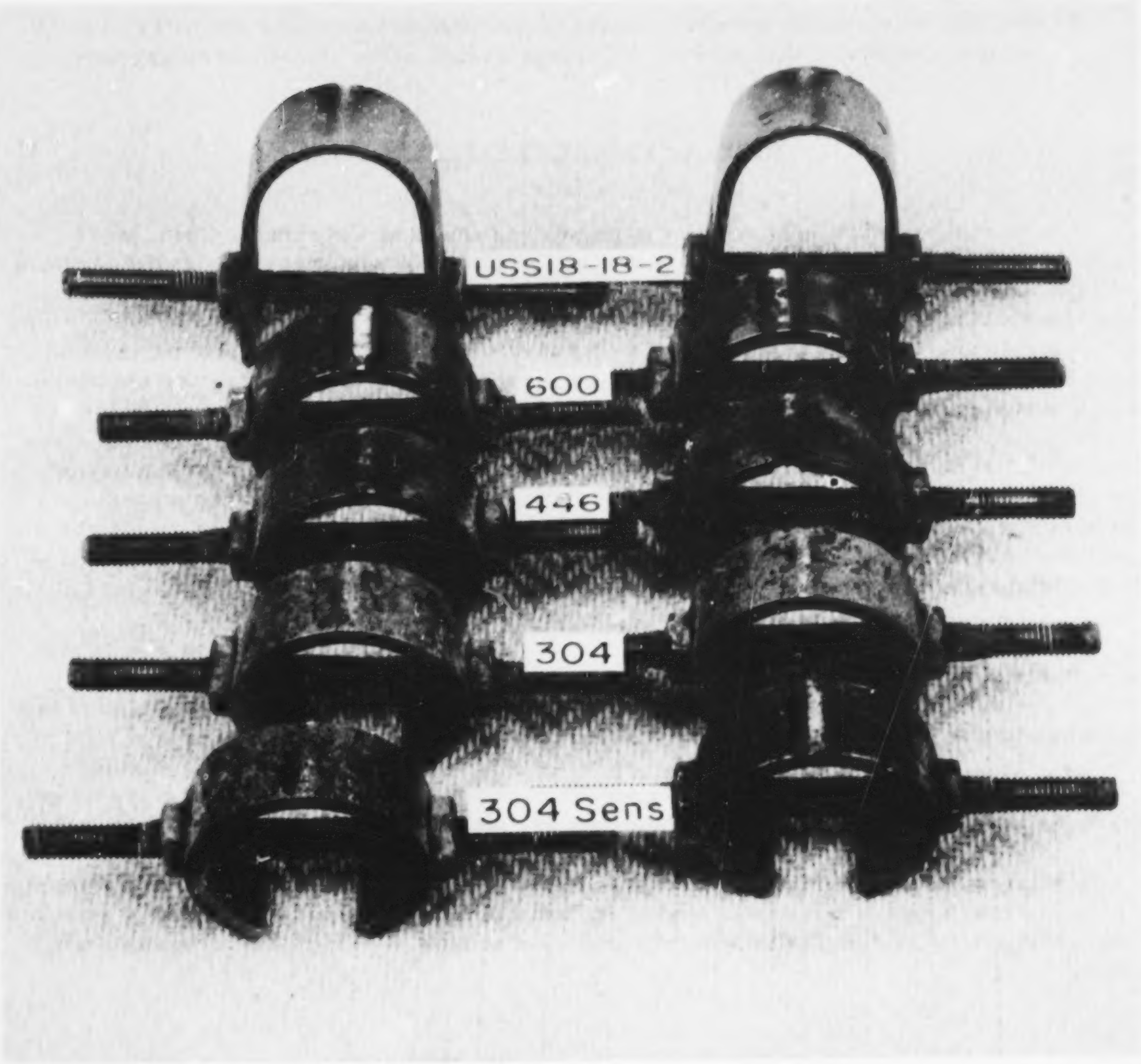


7X C4014
a. Specimen B-1

7X C4015
b. Specimen B-2

FIGURE 35. APPEARANCE OF INCONEL 600 STRESSED SPECIMENS AFTER EXPOSURE OF 63 DAYS IN INCINERATOR SCRUBBER EFFLUENT WATER


USS18-18-2
600
446
304
304 Sens

3923

FIGURE 36. APPEARANCE OF MORE SEVERELY CORRODED SPECIMENS FROM SCRUBBER AT NORTH MONTGOMERY COUNTY

The C-ring specimens were exposed for 129 days.
The USS-18-18-2 specimen was exposed for 33 days.

Type 304 stainless steel was similarly affected, except that more linear strings of pits were present.

Inconel 600 was usually severely attacked at corners and edges and crevices. It will be recalled, however, that stressed C-rings of this alloy showed deep grooves.

Results From Columbus, Ohio

The scrubber solutions used in the exposures made at Columbus, Ohio, were obtained from the scrubber effluent stream at the North Montgomery County Incinerator. The solutions were changed three times during the 137-day period. A set of specimens identical to those exposed at North Montgomery County was used. The specimens were completely submerged in the scrubber water contained in a large Pyrex jar maintained at 170-180 F. Air was slowly sparged through the solution during the exposure. The pH of the solutions was maintained at 2.0-2.5 by means of occasional additions of sulfuric or hydrochloric acids. Specimens were examined at 20, 42, 95, and 137 days. The results in Table 12 have been arranged and tabulated in a manner similar to that used for the specimens described in the preceding section. The following materials furnished the best resistance when rated on the basis of good performance in all configurations in which they were run: Ti6Al-4V, Hastelloy C, Inconel 625, Alloy S-816, and Hastelloy F, Hastelloy G, and Hastelloy C-276.

It will be noted that stress-corrosion cracking was found on the Type 304 panels and C-rings. Figure 38 shows a crack running across the panel on each side of the circular weld. The cracked C-rings are shown in Figure 39. Cracking was also noted at an area in the weld and base metal of the Type 316L panel.

Stress-accelerated corrosion (trenches) running across the face of the specimen was found for the Inconel 600 and 601 specimens, as illustrated in Figure 39.

Pitting occurred on many of the specimens as noted in Table 12. It will be noted in Table 12 that most of the panels which showed bad pitting were also severely attacked at the crevices under the Teflon spacers near the support holes in the corners of the panels.

Fan Deposit Studies at Columbus, Ohio

As was pointed out elsewhere in this report, there have been field service failures of induced-draft fans, particularly from SCC when austenitic stainless steels were used. Carbon steel fans have also corroded rapidly by general attack and by pitting. This subject has been explored here experimentally by subjecting C-rings and U-bends of various alloys to deposits taken from the fan housing at the incinerator at North Montgomery County.

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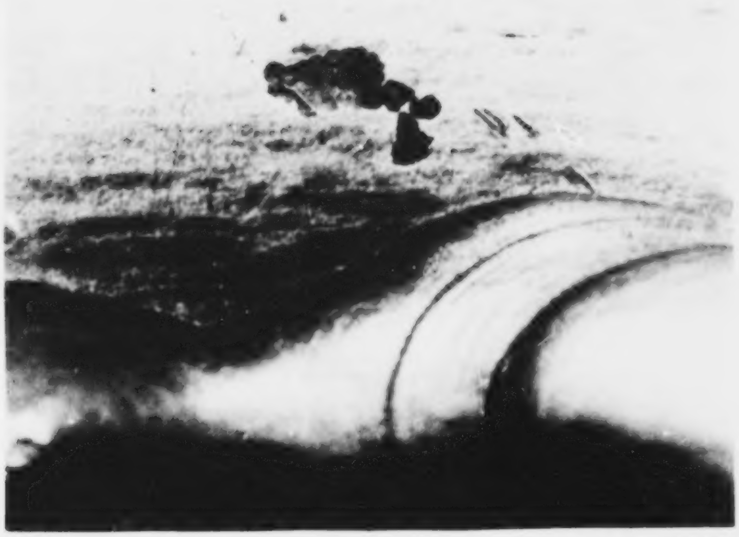


15X C4016

FIGURE 37. TYPICAL PITTING IN TYPE 316L PANEL EXPOSED AT NORTH MONTGOMERY COUNTY SCRUBBER FOR 129 DAYS

The pitting was worse in areas near the heat-affected zone adjacent to the weld.

TABLE 12. CORROSION RESULTS OF STRESSED AND WELDED SPECIMENS EXPOSED TO SCRUBBER SOLUTIONS AT COLUMBUS, OHIO[(a)]

Specimen				
Alloy	Number	Corrosion Results		
		U-Bends		
Ti-6Al-4V	J3	Good resistance, 137 days		
	J4	Good resistance, 137 days		
Hast C	D3	Good resistance, 137 days		
	D4	Good resistance, 137 days		
625	N3	Good resistance, 137 days		
	N4	Good resistance, 137 days		
Hast F	E3	Good resistance, 137 days		
	E4	Good resistance, 137 days		
Carp 20	C3	Good resistance, 137 days		
	C4	Good resistance, 137 days		
S816	F3	Good resistance, 137 days; surface mottled		
	F4	Good resistance, 137 days; surface mottled		
316L	H3	Slight stringer corrosion at edges, 41 days, same 137 days		
	H4	Good resistance, 137 days		
Hast G (welded)	S1	Good resistance, 66 days		
	S2	Good resistance, 66 days		
Hast C276 (welded)	R1	Good resistance, 66 days		
	R2	Good resistance, 66 days		
Ti75A	K3	Weld grains outlined 42 days; same 137 days, fine weld cracks		
	K4	Weld grains outlined 42 days; same 137 days, fine weld cracks		
Armco	T3	Edge pits, 33 days, same at 66 days		
22-13-5	T4	Edge pits, 33 days, same at 66 days		
USS	U3	Edge pits, 33 days, worse at 66 days, surface roughening		
18-18-2	U4	Edge pits 33 days, worse at 66 days		
		C-Rings		
825	A3	Good resistance, 137 days		
	A4	Good resistance, 137 days		
310	1J	Good resistance, 137 days		
	1K	Good resistance, 137 days		
316L	H3	Good resistance, 137 days		
	H4	Good resistance, 137 days		
600	B3	Fine pits, 42 days; trenches, pits across face, edge pits, 137 days		
	B4	Fine pits, 42 days; trenches, pits across face, edge pits, 137 days		
446	4J	Pitting at 20 days, more pitting at 137 days		
	4K	Pitting at 20 days, more pitting at 137 days		
601	M3	Bad edge pitting, 43 days, deep trenches and pits across face, 137 days		
	M4	Edge pitting, 95 days, trench formation, pitting, 137 days		
304	3J	One crack at 20 days, deep crack at 137 days, some small cracks		
	3K	Possible crack at pitted area, 137 days		
304	2J	Fine cracks at 95 days, same at 137 days		
Sens	2K	Three cracks at 20 days, complete penetration at one crack, 137 days		
		Circular Welded Plates		
			Depth of Attack, mils	
			Pit	Crevice
Ti-6Al-4V	J	Good resistance, 137 days; weld grains outlined	0	0
Hast C	D	Good resistance, 137 days	0	0
S816	F	Good resistance, 137 days; surface markings	0	0
625	N	Good resistance, 137 days	0	0
Hast F	E	Good resistance, 137 days	0	0
600	B	Roughened, pitted at 95 days; same at 137 days	3	0
Carp 20	C	Pits near weld, attack at crevice 95 days; same at 137 days	3	20
310	I	Pitted on back near weld, 42 days; attack at crevice, 137 days	5	48
825	A	Pits in weld, 95 days; pits front and back, 137 days	8	3
316 L	H	Pitting on back welded area, 42 days; more pitting, 137 days, crevice attack, crack in and near weld	7	12
Armco 22-13-5	T	Pits in and near weld, crevice attack, 33 days; same at at 55 days	3	7
304	G	Crack through plate near weld, 42 days; two bad cracks, 137 days	0	5

(a) pH 2.0-2.5
Temperature 170-180 F
Aerated
Most specimens examined at 20, 42, 95, and 137 days

Deposit Analyses

Deposits from both the blade and the housing of the induced-draft fan at the Montgomery County North Incinerator were analyzed during these studies. Results are summarized in Figure 40. These deposits were substantially different from those found on the corrosion probes at the Miami County and Norfolk incinerators. The difference results primarily from the fact that a wet scrubber has removed most of the particulate material from the gas stream before it reaches the induced-draft fan. As a result, the amount of iron, aluminum, silicon, and calcium found in the fan deposit is low. These are the components of the clay-like materials in the fly ash which were removed in the scrubber. The lead, zinc, and potassium content was high, and the compounds $K_2Pb(SO_4)_2$ and $K_2Zn(SO_4)_2$ were readily identifiable in the deposits by means of X-ray diffraction. The presence of these compounds in the fan deposits shows that some particles escape the scrubber water, as these sulfates are soluble but will precipitate as $PbSO_4$ when exposed to water.

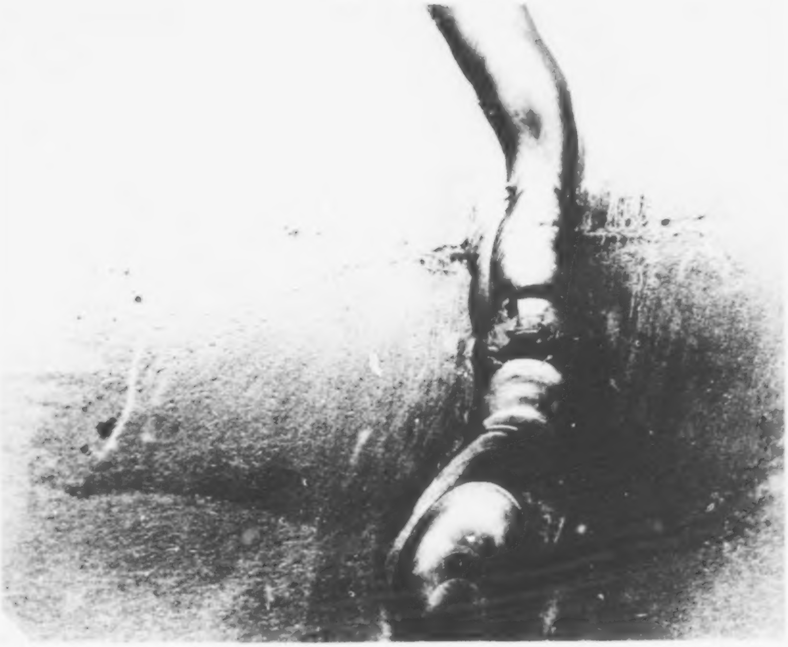
The chlorine content of these deposits was unusually high. In fact, the amount of chlorine found in the fan housing deposit was greater than that determined in any of the other bulk deposits analyzed on this program. The chloride concentration of almost 16 percent in the housing deposit would account for the severe attack by this deposit of various metals used in our laboratory experiments with the deposit as described later. This buildup of chloride in the ID fan deposits shows that the wet scrubber is not removing all the HCl vapors.

Corrosion

The stressed specimens were placed edge down and buried about one-half inch in the deposit, which was held several inches above a sample of scrubber solution. The entire assembly was contained in a closed vessel which opened at the top to take a reflux condenser. The scrubber solution was heated to 170-180 F to produce humid conditions within the container. Thus, the stressed samples touched damp deposit and vapors from the scrub water.

The results for the twelve alloys including carbon steel which were exposed up to 6 weeks are given in Table 13. Type 304 stainless steel and plain carbon steel were severely pitted after 2 weeks and were removed, while Armco 22-13-5 was severely cracked and removed at this time. The alloys have been arranged with the most resistant alloys at the top of the list and the least resistant to the bottom of the table. The degree of rusting, pitting, and cracking is indicated by numbers from 0-9. Pit depths are also shown. The best resistance was furnished by Ti-6Al-4V, Inconel 625, and Hastelloy C. A small amount of pitting was observed on the Type S-816, Incoloy 800, and Incoloy 825 specimens. Stress-corrosion cracking and pitting was detected by surface examination of the Carpenter 20, Type 316L, USS-18-18-2, and Armco 22-13-5 specimens.

It can be seen from the results just discussed that the corrosion under the humid fan deposits was more severe than in the scrubber water. This is undoubtedly related to the presence of localized high concentration of chloride salts at the metal surfaces and the absences of scale forming protective deposits.



15X C4017

FIGURE 38. SCC THROUGH TYPE 304 STAINLESS STEEL PLATE AND WELD

This panel was exposed in the scrubber solution at Columbus for 137 days. A crack was first observed after 42 days.

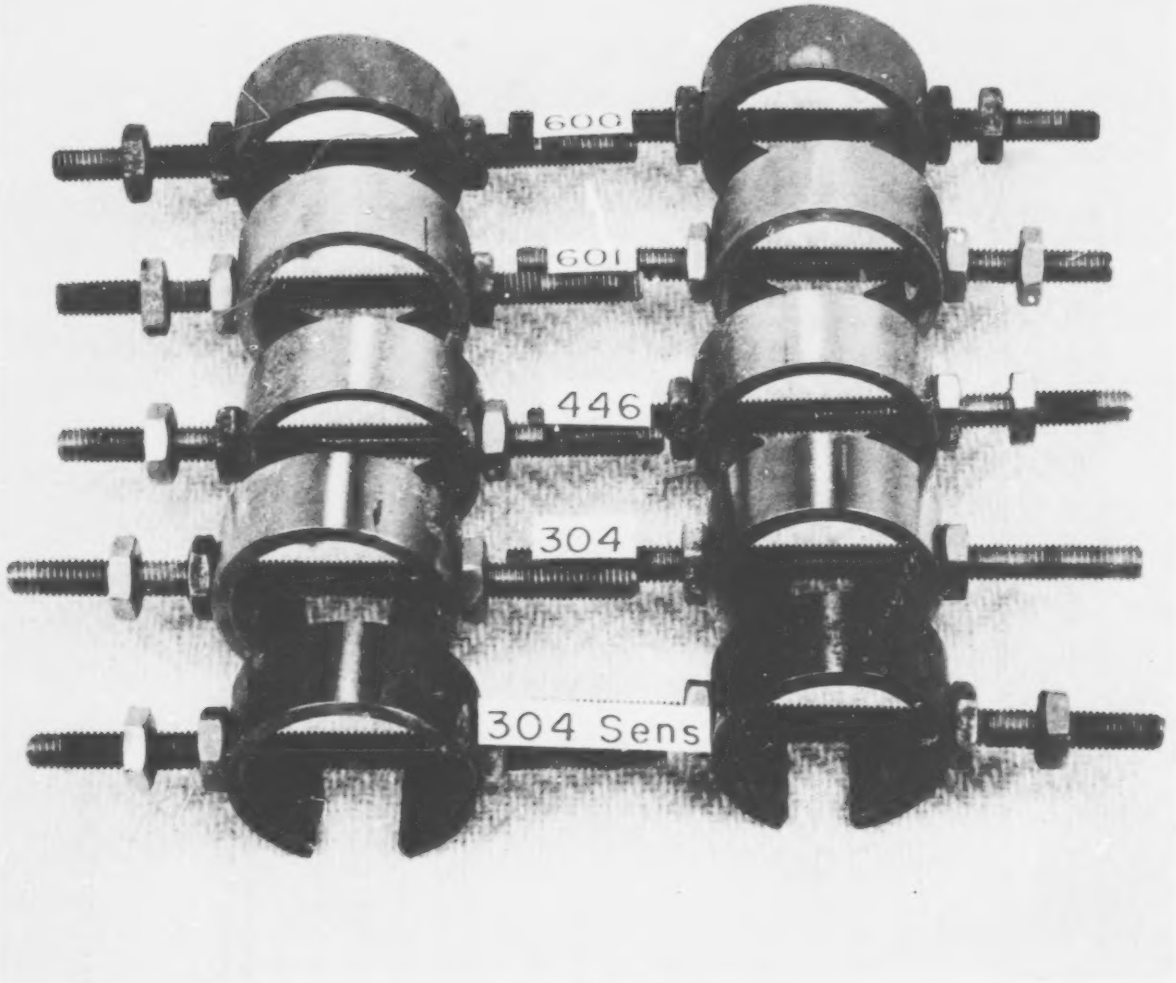


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FIGURE 39. APPEARANCE OF CORRODED C-RING SPECIMENS AFTER EXPOSURE TO SCRUBBER SOLUTIONS AT COLUMBUS, OHIO

Stress corrosion cracking has occurred in the Type 304 and 304 sens pieces. Grooves are visible on the Inconel pieces.

TABLE 13. CORROSION RESULTS OF STRESSED SPECIMENS EXPOSED TO INDUCED DRAFT FAN HOUSING DEPOSITS UNDER HOT HUMID CONDITIONS

Alloy Type	Specimen	Corrosion$^{(a)}$ Found at Indicated Week					Pit Depth, mils
		1	2	3	4	6	
Ti-6Al-4V	J	G-0, P-0, C-0	G-0, P-0 C-0	G-0, P-0, C-0	G-0, P-0, C-0	G-1, P-0, C-0	0
Inconel 625	N	G-0, P-0, C-0	--	G-0, P-0, C-0	G-0, P-0, C-0	G-0, P-0, C-0	0
Hastelloy C	D	G-0, P-0, C-0	G-0, P-0, C-0	G-0, P-0, C-0	G-1, P-0, C-0	G-1, P-0, C-0	0
S 816	F	G-0, P-1, C-0	--	G-0, P-1, C-0	G-1, P-2$^{(b)}$, C-0	G-1, P-2$^{(b)}$, C-0	2
Incoloy 800	W	G-1, P-1, C-0	--	G-1, P-1, C-0	G-1, P-1, D-2, C-0	G-1, P-2, D-3, C-0	6
Incoloy 825	A	G-0, P-2$^{(b)}$, C-0	G-0, P-3$^{(b)}$, C-0	G-0, P-3$^{(b)}$, C-0	G-0, P-3$^{(b)}$, C-0	G-0, P-4$^{(b)}$, D-2$^{(b)}$, C-0	15
Carpenter 20	C	G-0, P-2$^{(b)}$, C-0	--	G-0, P-2$^{(b)}$, C-0	G-0, P-2$^{(b)}$, D-2$^{(b)}$, C-1$^{(b)}$	G-0, P-3$^{(b)}$, D-3$^{(b)}$, C-1$^{(b)}$	9
316L	H	G-1, P-4, D-2 C-0	G-1, P-4, D-2 C-0	G-2, P-4, D-3, C-1	G-2, P-4, D-3, C-1	G-2, P-4, D-4, C-2	16
USS-18-18-2	U	G-3, P-3, C-0	G-4, P-3, C-0	G-5, P-4, C-0	G-5, P-4, C-1	G-6, P-4, D-1, C-2	7
Armco 22-13-5	T	G-1, P-3, C-7	G-1, P-3, C-8	(removed)	--	--	8
304	G	G-5, P-5, C-0	G-8, P-5, C-0	(removed)	--	--	--
Plain-Carbon Steel	V	G-8	G-9 (removed)	--	--	--	--

(a) Magnitude of corrosion increasing 0-9 by surface examination.

G = General Rust
P = Surface Pitting
D = Deep Pitting
C = Cracking

(b) Major attack where specimens contact deposits.

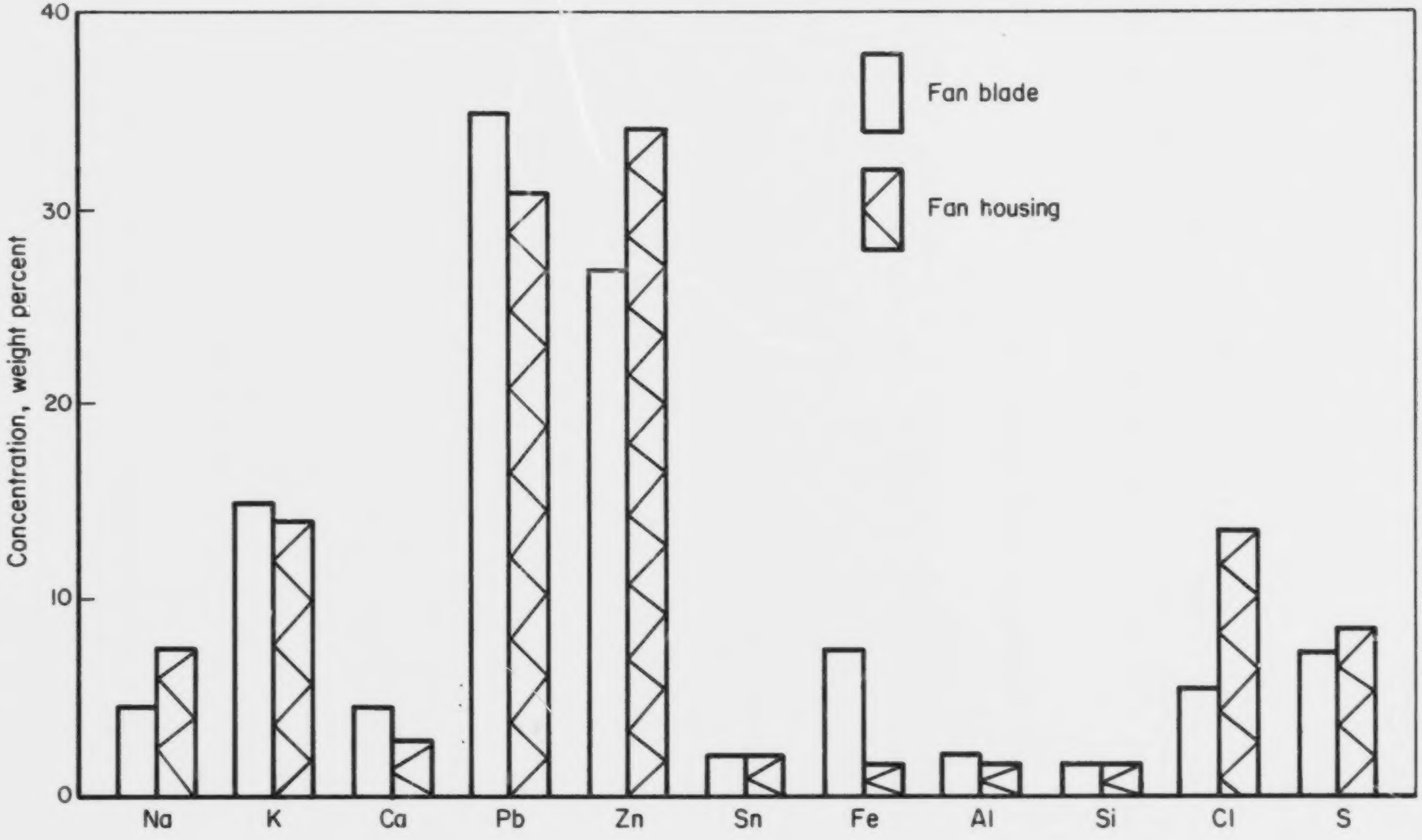

FIGURE 40. COMPOSITION OF DEPOSITS ON INDUCED-DRAFT FAN – MONTGOMERY COUNTY NORTH INCINERATOR

The most severe surface cracking was observed on Armco 22-13-5. More rusting and pitting took place on the USS 18-18-2 alloy, although cracks were seen in the face view at 7X.

The examination of cross sections was required in some cases to reveal the SCC. This was either because of the presence of severe rusting, which masked the cracks as for Type 304, or because the cracks were small, as for Type 316L and Carpenter 20.

It will be noted that the depth of the cracks in the alloy just mentioned when viewed in cross section was about 40 mils. Similar penetration of stress-corrosion cracks was observed with Type 316L stainless steel. However, in this case less surface rusting occurred. The depth of the attack on the Carpenter 20 specimen was only about 5 mils.

Conclusions From Scrubber Studies

The studies of alloys under three scrubber exposure conditions have furnished useful information on their general corrosion and stress-corrosion cracking behavior.

(1) The superior resistivities of Ti-6Al-4V, Inconel 625, and Hastelloy C as reported by other investigators (such as the International Nickel Company) have been confirmed. Unalloyed Titanium 75A may also be good, but since some fine cracks in the weld were visible it has been rated lower. It is possible that these cracks were present in the as-welded material.

Hastelloy F and S-816 have also shown good resistance, as have Hastelloy G (welded) and Hastelloy C-276 (welded). The last two alloys were exposed for only 66 days, however.

(2) The studies indicate that the alloys mentioned in the above paragraphs are also resistant to stress-corrosion cracking under the conditions used.

(3) Conditions present when metals are in contact with ID fan deposits are more likely to produce stress-corrosion cracking than are the conditions present in scrubber waters. Thus, the stainless steels – Types 304, 316L, USS 18-18-2, Armco 22-13-5, and Carpenter 20 – were cracked to varying degrees when in contact with these deposits.

In scrubber solutions, on the other hand, Types 304 and 316L were the only materials that cracked. This was true for both sensitized and unsensitized Type 304 material. It is significant, however, that stress apparently had a marked effect on the corrosion of Inconel 600 and 601 in scrubber solutions because deep grooves are produced in stressed area.

Pitting and crevice attack seemed to be a more severe problem with many alloys in the hot scrubber solutions. For example, pitting was noted on Type 304, 310, 316L, 446, Carpenter 20, USS-18-18-2, Armco 22-13-5, and Incoloy 825. The leakage seen in some scrubbers constricted of 316L stainless steel reflects the pitting tendency of this alloy in scrubber environments.

No preferential attack was noted at crevices where the C-rings or U-bends touched. However, severe attack as noted in the tables was found with many alloys at areas under the Teflon spacers near the corner holes in the 4 x 4-inch panels.

Because of the cost of the more corrosion-resistant materials for incinerator scrubber service, it appears that consideration should be given to the use of nonmetallic construction materials as suggested by Ellison and Kempner.(83, 84, 85) The good performance of such materials at the East 73rd Street Incinerator also is an important consideration.

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PUBLICATIONS RESULTING FROM THE RESEARCH

- Discussions on Paper, "Considerations in the Construction of Large Refuse Incinerators", by F. Nowak, National Incinerator Conference, 1970.

- Miller, Paul D., and Krause, Horatio H., "Fireside Metal Wastage in Municipal Incinerators", ASME Paper 70-WA/Inc-2, Annual Meeting, New York City, December, 1970.

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- Miller, Paul D., and Boyd, Walter K., "Corrosion in Wet Scrubbers in Municipal Incinerators", presented at North Central Regional Conference NACE, Charleston, West Virginia, October 27, 1971.

- Miller, Paul D., "Incinerator Corrosion", presented at Engineering Research Foundation Conference, Deerfield, Massachusetts, August 23-27, 1971.

- Miller, Paul D., and Krause, Horatio H., "Corrosion of Carbon and Stainless Steels in Flue Gases from Municipal Incinerators", submitted to ASME for the June, 1972, National Incinerator Conference.

- Miller, Paul D., Krause, Horatio H., Vaughan, Dale A., and Boyd, Walter K., "The Mechanism of High-Temperature Corrosion in Municipal Incinerators" submitted to NACE.

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APPENDIX

Probe-Specimen Handling

The 34 corrosion specimens were separated from each other by tapping with a fiber mallet. The amount of metal wastage was determined by chemically or electrochemically stripping the residual deposits and scale from the majority of the specimens using standard procedures.(86) The laboratory specimens of T11 and A106 were stripped in Clarkes Solution: 100 g conc HCl, 2 g Sb_2O_3, 5 g $SnCl_2$ at room temperature. Most specimens were stripped cathodically in 10 percent H_2SO_4 containing 1-ethylquinolinium iodide inhibitor.

Some stainless steel specimens were descaled in a two-step process: first with 11 percent NaOH and 5 percent $KMnO_4$ at 212 F and then with 20 percent HNO_3 with 2 percent HF at 130 F. Then the weight loss and dimensional changes were measured. The original weights of these specimens were in the range of 65 to 80 grams.

Experimental Results

Miami County

Tables A-1, A-2, and A-3 present wastage data by weight loss and penetration for Probes 1, 2, 3, 4, 5, 6, 7, 9, 12, 13, 14, and 15.

Norfolk

Table A-4 presents wastage data for Probes 8, 10, and 11 exposed at Norfolk.

Laboratory

Tables A-5 and A-6 present corrosion results for studies made in the laboratory at 1000 F and 800 F, respectively.

Tables A-7, A-8, and A-9 present corrosion results for 600 F for steels A-106, T11, and Type 321, respectively.

TABLE A-1. TUBE WASTAGE ON MIAMI COUNTY PROBES

Probe 1 (312 hr)				Probe 2 (389 hr)				Probe 3 (323 hr)				Probe 4 (122 hr)			
	Wt Loss[a],	Wastage			Wt Loss,	Wastage			Wt Loss,	Wastage			Wt Loss,	Wastage	
Specimen	grams	Mils	Mils/Month	Specimen	grams	Mils	Mils/Month	Specimen	grams	Mils	Mils/Month	Specimen	grams	Mils	Mils/Month
A106-1	3.7	4.8	11	A106-1	3.9	5.2	10	A106-1	–	8.0[b]	18	A106-1	1.6	2.1	13
T11-2	5.3	6.9	16	T11-2	5.0	6.5	12	T11-2	4.6	5.5	12	T11-2	3.9	5.1	31
A106-3	4.3	5.6	13	A106-3	5.2	6.8	13	A106-3	5.4	7.1	16	A106-3	3.7	4.9	29
T11-4	–	5.6[b]	13	T11-4	7.5	9.9	19	T11-4	3.8	5.0	11	T11-4	4.1	5.4	32
A106-5	6.5	8.4	20	A106-5	7.1	9.4	18	A106-5	–	9.0[b]	20	A106-5	3.7	4.9	29
T11-6	9.4	12.2	29	T11-6	5.6	7.3	14	T11-6	–	10.0[b]	23	T11-6	8.4	11.1	66
A106-7	6.6	8.5	20	A106-7	6.6	8.6	16	A106-7	5.8	7.7	17	A106-7	4.3	5.7	34
T11-8	16.4	21.4	50	T11-8	6.7	8.8	17	T11-8	6.0	7.9	18	321-8	1.9	2.5	15
A106-9	9.3	12.1	28	A106-9	5.6	7.4	14	A106-9	4.3	5.7	13	304-9	1.9	2.5	15
T11-10	13.9	18.1	42	T11-10	5.3	8.0	15	T11-10	–	–	–	T11-10	4.5	5.9	35
A106-11	–	16.8[b]	39	A106-11	–	10.0[b]	19	A106-11	6.2	8.2	19	A106-11	3.9	5.1	31
T11-12	–	14.3[b]	33	T11-12	–	21.0[b]	30	T11-12	7.4	9.8	22	T11-12	5.0	6.6	40
A106-13	10.0	13.1	31	A106-13	8.6	11.2	21	A106-13	6.7	8.9	20	A106-13	6.1	8.0	48
T11-14	13.6	17.7	42	T11-14	11.6	15.1	28	T11-14	10.0	13.2	30	T11-14	6.9	9.1	55
A106-15	10.2	13.3	31	A106-15	11.0	14.3	27	A106-15	–	12.0[b]	27	304-15	1.3	1.7	10
T11-16	19.1	24.8	58	T11-16	14.7	19.3	36	T11-16	10.2	13.5	30	321-16	3.5	4.6	28
A106-17	9.1	11.9	28	A106-17	12.2	16.1	30	A106-17	10.8	14.3	32	A106-17	6.5	8.6	52
T11-18	–	16.0[b]	37	T11-18	14.9	19.4	36	T11-18	13.8	18.2	41	T11-18	9.1	12.0	72
304-19	5.2	6.8	16	304-19	5.4	7.0	13	321-19	5.1	6.7	15	A106-19	6.7	8.9	54
A106-20	13.2	17.2	40	A106-20	13.6	17.7	33	A106-20	12.4	16.4	37	321-20	4.1	5.4	32
304-21	4.4	5.7	13	304-21	5.4	7.0	13	321-21	8.6	11.3	25	304-21	2.5	3.3	20
321-22	9.3	12.1	28	321-22	10.6	13.8	26	304-22	8.7	11.5	26	321-22	4.5	5.9	35
304-23	5.1	6.6	15	304-23	7.6	9.9	19	321-23	15.2	20.0	45	304-23	3.8	5.0	30
321-24	11.4	15.0	35	321-24	12.1	16.0	30	304-24	10.7	14.1	32	321-24	4.5	5.9	35
304-25	7.3	9.5	22	304-25	7.3	9.5	18	321-25	–	16.0[b]	36	304-25	3.9	5.2	31
321-26	10.7	13.9	33	321-26	14.4	18.7	35	304-26	11.7	15.4	35	321-26	4.1	5.4	32
304-27	5.7	7.4	17	304-27	8.8	11.6	22	321-27	17.6	23.2	52	304-27	4.7	6.2	37
321-28	–	10.0[b]	23	321-28	14.1	18.3	34	304-28	12.3	16.1	36	321-28	4.5	5.9	35
304-29	–	6.0[b]	14	304-29	8.5	11.0	21	321-29	18.8	24.8	56	304-29	5.0	6.6	40
321-30	7.5	9.7	23	321-30	13.4	17.7	33	304-30	12.1	16.0	36	321-30	6.1	8.0	48
304-31	6.0	7.8	18	304-31	9.3	12.1	23	321-31	16.1	21.2	48	304-31	4.8	6.3	38
321-32	11.6	15.1	35	321-32	14.8	19.5	36	304-32	11.9	15.7	35	321-32	5.4	7.1	43
321-33	7.1	9.2	22	304-33	–	13.0[b]	24	321-33	20.2	26.6	60	304-33	4.9	6.5	39
304-34	11.5	14.9	35	321-34	–	19.0[b]	36	304-34	7.8	10.3	23	321-34	5.2	6.9	41

(a) Adjusted from micrometer measurements, where appropriate.

(b) Based on metallography.

TABLE A-2. TUBE WASTAGE ON MIAMI COUNTY PROBES

Probe 5 (190 hr)				Probe 6 (218 hr)				Probe 7 (101 hr)				Probe 9 (828 hr)			
	Wt Loss,	Wastage			Wt Loss,	Wastage			Wt Loss,	Wastage			Wt Loss,	Wastage	
Specimen	grams	Mils	Mils/Month	Specimen	grams	Mils	Mils Month	Specimen	grams	Mils	Mils Month	Specimen	grams	Mils	Mils Month
A106-1	1.9	2.5	10	A106-1	3.8	5.0	17	A106-1	3.0	4.0	29	A106-1	–	–	–
T11-2	3.6	4.8	18	T11-2	6.4	8.4	28	T11-2	4.3	5.7	41	T11-2	2.7	3.6	3.2
A106-3	7.1	9.4	36	A106-3	5.7	7.5	25	A106-3	8.2	10.8	78	A106-3	3.4	4.5	4.0
T11-4	9.5	12.5	48	T11-4	8.5	11.2	37	T11-4	13.3	17.5	126	T11-4	4.1	5.4	4.9
A106-5	14.1	18.1	69	A106-5	7.8	10.3	34	310-5	1.6	2.1	15	A106-5	4.7	6.2	5.5
T11-6	15.8	20.8	79	T11-6	8.4	11.1	37	316-6	5.9	7.8	56	T11-6	4.9	6.4	5.6
304-7	5.5	7.2	27	A106-7	7.8	10.3	34	446-7	1.5	2.0	14	446-7	2.4	3.2	2.8
321-8	8.0	10.5	40	321-8	2.9	3.8	13	T11-8	12.3	16.2	117	321-8	3.4	4.5	4.0
A106-9	21.4	28.3	107	304-9	1.8	2.4	8	A106-9	12.4	16.4	119	304-9	3.1	4.1	3.6
T11-10	21.0	27.6	105	T11-10	8.7	11.5	38	310-10	4.1	5.4	39	310-10	–	–	–
304-11	11.3	14.9	57	A106-11	7.9	10.4	34	316-11	5.9	7.8	56	316-11	4.0	5.3	4.7
T11-12	23.5	31.0	118	T11-12	8.3	11.0	36	446-12	3.4	4.5	33	T11-12	6.6	8.7	7.7
304-13	11.3	14.9	57	A106-13	7.9	10.4	34	304-13	5.5	7.2	52	A106-13	6.8	8.9	7.9
321-14	11.0	14.5	55	T11-14	9.6	12.7	42	310-14	5.9	7.8	57	T11-14	8.5	11	10
304-15	7.5	9.9	38	304-15	2.5	3.3	11	316-15	4.8	6.3	46	A106-15	11.0	15	13
321-16	7.4	9.7	37	321-16	5.8	7.7	25	446-16	2.0	2.6	19	321-16	8.0	11	9
304-17	3.6	4.7	18	A106-17	9.4	12.4	41	310-17	3.3	4.3	31	304-17	5.8	7.7	6.8
321-18	5.6	7.4	28	T11-18	10.3	13.6	45	316-18	2.9	3.8	28	T11-18	17.3	23	20
304-19	4.0	5.3	20	A106-19	13.2	17.4	57	446-19	1.5	1.9	14	A106-19	–	24(b)	21
				321-20	6.2	8.2	27					321-20	11.2	15	13
				304-21	7.5	9.9	33					304-21	–	–	–
				321-22	8.3	11.0	36					446-22	4.6	6.1	5.4
				304-23	7.7	10.2	34					310-23	6.5	8.6	7.6
				321-24	10.7	14.1	47					316-24	17.3	23	2.0
				304-25	8.3	11.0	36					321-25	–	21(b)	19
				321-26	8.6	11.3	37					304-26	9.5	13	11
				304-27	8.2	10.8	36					446-27	–	–	–
				321-28	11.1	14.1	47					310-28	5.9	7.8	6.9
				304-29	10.3	13.6	45					316-29	17.1	23	20
				321-30	12.4	16.4	54					321-30	18.1	24	21
				304-31	7.8	10.3	34					304-31	12.4	16	15
				321-32	15.5	20.4	67					446-32	7.7	10	9.0
				304-33	9.2	12.1	40					310-33	6.7	8.8	7.8
				321-34	13.9	18.3	60					316-34	–	–	–

TABLE A-3. TUBE WASTAGE ON MIAMI COUNTY PROBES

Probe 12 Miami County (492 Hr)				Probe 13 Miami		County (206 Hr)		Probe 14 Miami County (420 Hr)				Probe 15 Miami County (291 Hr)			
	Wt. Loss,	Wastage			Wt. Loss,	Wastage			Wt. Loss,	Wastage			Wt. Loss,	Wastage	
Specimen	grams	Mils	Mils/Month	Specimen	grams	Mils	Mils/Month	Specimen	grams	Mils	Mils/Month	Specimen	grams	Mils	Mils/Month
A106W-1	3.1	4.1	6.1	A106-1	3.1	4.1	14.6	A106-1	5.8	7.7	14.7	A106-1	8.2	9.7	24.2
A106-570W-2	7.5	9.5	13.4	Al-2	0.2	0.8	2.8	446-2	4.5	5.9	11.2	446-2	3.4	4.5	11.3
A106-570+W-3	4.1	5.5	8.1	T11-3	5.0	6.6	23.4	T11-3	12.4	13.9	26.4	416-3	12.3	15.5	38.7
A106Al-4	3.2	4.2	6.2	A106-4	5.6	7.4	26.2	A106-4	11.9	15.7	29.8	T11-4	41.1	32.0	80.0
A106Cr-5	3.4	4.6	6.8	Al-5	Fail	--	--	446-5	4.5	5.9	11.2	A106Cr-5	23.2	9.0	22.5
T11W-6	6.3	8.3	12.3	T11-6	5.6	7.4	26.2	T11-6	17.1	20.6	38.2	416-6	34.0	39.0	98.0
T11-570W-7	7.9	10.4	15.4	In600-7	1.9	2.5	8.8	In600-7	3.0	4.0	7.6	A106Al-7	37.2	32.2	80.5
T11-570+W-8	8.3	11.0	16.1	In601-8	1.2	1.6	5.7	In601-8	1.4	1.8	3.4	416-8	37.0	48.8	122.0
T11-9	13.6	18.0	26.6	In825-9	1.9	2.5	8.8	In825-9	2.0	2.6	4.9	446-9	3.6	4.7	11.7
A106-10	13.5	17.8	26.3	310-10	2.1	2.8	9.9	310-10	4.2	5.5	10.5	310-10	5.9	3.2	8.0
A106W-11	4.8	5.7	8.4	A106-11	5.3	7.0	24.8	A106-11	17.3	21.0	40.0	304-11	8.6	7.6	19.0
A106-570W-12	14.9	19.3	28.5	T11-12	5.5	7.3	25.8	446-12	Met.	--	11.4	416-12	Large	--	--
A106-570+W-13	19.7	23.4	34.6	In600-13	3.2	4.2	14.9	In600-13	Met.	--	46.3	A106W-13	Large	--	--
A106Al-14	7.6	8.0	11.9	In601-14	0.6	0.8	2.8	In601-14	Met.	--	36.4	A106-570W-14	Large	--	--
A106Cr-15	8.6	9.3	13.8	In825-15	1.4	1.9	6.7	In825-15	Met.	--	17.8	A106-570+W-15	Large	--	--
T11W-16	11.0	11.8	17.5	310-16	1.5	2.0	7.1	310-16	Met.	--	11.0	416-16	Large	--	--
T11-570W-17	14.9	18.3	27.0	A106-17	13.1	17.3	61.1	A106-17	26.3	24.2	45.8	T11-17	Large	--	--
T11-570+W-18	14.0	17.0	25.2	T11-18	24.1	32.0	111.3	310-18	2.6	3.4	6.5	A106Cr-18	Large	--	--
T11-19	20.5	25.6	38.0	In600-19	7.4	9.8	34.6	In600-19	8.3	11.0	21.0	304-19	3.7	4.9	12.2
A106-20	18.1	17.3	25.6	In601-20	1.4	1.9	6.7	In601-20	26.9	35.5	67.5	A106W-20	Large	--	--
A106W-21	7.6	8.0	12.0	In825-21	4.1	5.4	19.1	In825-21	11.6	15.3	29.0	A106-570W-21	Large	--	--
A106-570W-22	17.1	19.9	29.4	A106-22	18.1	23.9	84.4	A106-22	31.9	30.0	57.0	A106-570+W-22	Large	--	--
A106-570+W-23	18.8	20.5	29.7	T11-23	26.9	35.5	126.1	446-23	6.1	8.1	15.4	416-23	Large	--	--
304-24	8.5	11.3	16.5	304-24	6.5	8.6	32.1	304-24	10.0	13.0	24.6	T11W-24	Large	--	--
446-25	2.5	2.0	3.0	316-25	4.4	5.8	20.6	316-25	8.6	11.2	21.2	T11-570W-25	Large	--	--
310-26	6.9	8.0	11.9	321-26	9.7	12.8	45.2	321-26	17.4	22.6	43.0	T11-570+W-26	Large	--	--
316-27	9.6	11.6	17.3	446-27	3.9	5.1	18.0	310-27	7.2	9.5	18.0	321-27	19.2	18.6	46.5
321-28	14.0	17.9	26.4	310-28	10.7	14.1	50.0	446-28	7.6	10.0	19.0	304-28	11.7	13.3	33.2
T11W-29	15.1	15.8	23.3	In600-29	33.6	44.5	158.0	In600-29	40.3	Large	Large	310-29	7.1	9.4	23.6
T11-570W-30	20.2	21.1	31.2	In601-30	19.9	26.3	93.0	In601-30	38.4	Large	Large	316-30	8.9	9.8	24.5
T11-570+W-31	17.8	20.0	30.0	In825-31	6.3	8.3	29.4	In825-31	10.3	13.6	25.8	446-31	11.6	7.5	18.7
A106Al-32	9.0	12.0	20.0	304-32	7.1	9.4	33.3	304-32	12.5	16.3	31.0	In601-32	Large	--	--
A106Cr-33	18.4	17.0	25.0	316-33	6.0	7.9	28.0	316-33	9.8	12.9	24.5	In825-33	10.2	13.5	33.8
310-34	4.1	4.9	7.2	321-34	11.1	14.6	51.6	446-34	2.9	3.9	7.4	416-34	18.3	21.2	53.0

TABLE A-4. TUBE WASTAGE ON NORFOLK PROBES

Probe 8 (180 hr)				Probe 10 (168 hr)				Probe 11 (1318 hr)			
Specimen	Wt Loss, grams	Wastage		Specimen	Wt Loss, grams	Wastage		Specimen	Wt Loss grams	Wastage	
		Mils	Mils/Month			Mils	Mils/Month			Mils	Mils/Month
A106-1	2.9	3.8	15	A106-1	1.2	1.6	6	A106-1	4.2	5.5	3.0
A11-2	3.9	5.1	21	T11-2	-	-	-	T11-2	7.6	10.0	5.5
A106-3	3.9	5.1	21	A106-3	1.3	1.7	7	A106Al-3	1.7	2.2	1.2
T11-4	3.4	4.5	18	T11-4	1.0	1.3	5	T11-4	9.5	12.5	6.9
A106-5	3.1	4.1	17	A106-5	-	-	-	A106-5	10.5	13.8	7.6
T11-6	2.2	2.9	12	T11-6	1.1	1.3	5	A106Al-6	1.5	2.0	1.1
446-7	1.7	2.2	9	446-7	0.5	0.7	3	446-7	1.9	2.5	1.4
321-8	2.0	2.6	11	321-8	-	-	-	A106Cr-8	1.4	1.8	1.0
304-9	1.7	2.2	9	304-9	0.8	1.0	4	304-9	3.7	4.8	2.6
310-10	0.8	1.1	4	310-10	0.5	0.7	3	310-10	2.5	3.3	1.8
316-11	1.3	1.7	7	316-11	0.8	1.0	4	316-11	5.0	6.6	3.6
T11-12	2.1	2.8	11	T11-12	1.6	2.1	8	A106Al-12	1.2	1.6	0.9
A106-13	2.1	2.8	11	A106-13	-	-	-	A106-13	5.2	6.9	3.8
T11-14	2.3	3.0	12	T11-14	1.7	2.2	9	T11-14	8.0	10.5	5.8
A106-15	3.2	4.2	17	A106-15	2.0	2.6	10	A106-15	7.2	9.5	5.3
321-16	1.1	1.5	6	321-16	0.6	0.8	3	A106Cr-16	-	-	-
304-17	1.1	1.5	6	304-17	0.6	0.8	3	304-17	3.3	4.3	2.4
T11-18	2.7	3.6	15	T11-18	2.5	3.3	13	A106Al-18	2.1	2.8	1.5
A106-19	3.4	4.4	18	A106-19	-	-	-	A106-19	9.5	12.6	7.0
321-20	0.9	1.2	5	321-20	1.0	1.3	5	A106Cr-20	1.8	2.4	1.3
304-21	1.1	1.5	6	304-21	0.2	0.3	1	304-21	3.4	4.5	2.5
446-22	0.6	0.8	3	446-22	0.2	0.3	1	446-22	1.2	1.6	0.9
310-23	0.4	0.5	2	310-23	0.3	0.4	2	310-23	1.8	2.3	1.3
316-24	1.4	1.8	8	316-24	0.2	0.3	1	316-24	8.8	11.6	6.4
321-25	1.6	2.1	9	321-25	0.6	0.8	3	321-25	4.4	5.8	3.2
304-26	1.0	1.3	5	304-26	0.1	0.1	0.4	304-26	4.1	5.4	3.0
446-27	0.5	0.7	3	446-27	0.04	0.04	0.1	446-27	0.8	1.0	0.6
310-28	0.3	0.4	2	310-28	0.2	0.3	1	310-28	1.4	1.9	1.0
316-29	2.3	3.0	12	316-29	0.4	0.5	2	316-29	12.0	15.7	8.6
321-30	2.0	2.6	11	321-30	-	-	-	321-30	5.8	7.6	4.2
304-31	1.3	1.7	7	304-31	0.3	0.4	2	304-31	4.9	6.4	3.5
446-32	0.4	0.5	2	446-32	0.8	1.0	4	446-32	0.8	1.1	0.6
310-33	0.3	0.4	2	310-33	0.1	0.1	0.4	310-33	1.5	2.0	1.1
316-34	2.2	2.9	12	316-34	0.7	0.9	4	316-34	3.9	5.1	2.8

TABLE A-5. LABORATORY CORROSION RESULTS AT 1000 F

Run	Atmosphere	Corrosion Mixture, percent					Weight Loss[(a)], mg		Calculated Corrosion Rate[(b)], mils per month		Azide Test Results
		K_2SO_4	Na_2SO_4	NaCl	KCl	Fe_2O_3	Specimen 1	Specimen 2	Specimen 1	Specimen 2	
				A 106 – Grade B Steel							
0	F.G.[(c)]			–	–	–	109	110	8	8	neg
3	F.G.	59	16	–	–	25	80	84	5	6	+?
1	F.G.	58	16	1	–	25	211	507	14	34	++
5	F.G.	78	21	1	–	–	1074	1148	71	76	+++
20	F.G.	78	21	1	–	–	474	992	31	66	++
7	F.G.	99	–	1	–	–	281	299	19	20	+
10	F.G.	75	20	5	–	–	1003	1055	66	70	+++
11	F.G.	75	20	–	5	–	489	574	32	38	+++
13	F.G.	–	–	100	–	–	403	508	27	34	+++
15	F.G. No SO_2	–	–	100	–	–	192	146	13	10	neg
16	F.G. No SO_2	78	21	1	–	–	236	235	16	16	neg
18	F.G. No SO_2	78	21	1	–	–	307	293	20	19	neg
17	Helium	78	21	1	–	–	56	87	4	6	neg
19	Helium + 2500 ppm SO_2	78	21	1	–	–	362	360	24	24	neg
21	F. G. with 2500 ppm SO_2	75	20	5	–	–	1327	1675	88	111	+++
				A 213 – Grade T11 Steel							
0	F.G.	–	–	–	–	–	58	76	4	6	neg
3	F.G.	59	16	–	–	25	65	66	4	4	+?
1	F.G.	58	16	1	–	25	995	1060	60	70	++
5	F.G.	78	21	1	–	–	882	986	58	65	+++
20	F.G.	78	21	1	–	–	704	607	47	40	++
7	F.G.	99	–	1	–	–	270	268	18	18	+
10	F.G.	75	20	5	–	–	989	863	66	57	+++
11	F.G.	75	20	–	5	–	536	562	36	37	+++
13	F.G.	–	–	100	–	–	1243	1159	82	77	+++
15	F.G. No SO_2	–	–	100	–	–	142	113	9	8	neg
16	F.G. No SO_2	78	21	1	–	–	143	148	10	10	+?
18	F.G. No SO_2	78	21	1	–	–	120	104	8	7	neg
17	Helium	78	21	1	–	–	176	158	12	11	neg
19	Helium + 2500 ppm SO_2	78	21	1	–	–	406	404	27	27	neg
21	F. G. + 2500 ppm SO_2	75	20	5	–	–	1112	955	74	63	+
				Type 321 Stainless Steel							
0	F.G.	–	–	–	–	–	<1	<1	0	0	neg
3	F.G.	59	16	–	–	25	13	9	1	1	neg
1	F.G.	58	16	1	–	25	61	123	4	8	++
5	F.G.	78	21	1	–	–	287	160	19	11	+++
20	F.G.	78	21	1	–	–	217	280	14	19	+
7	F.G.	99	–	1	–	–	17	10	1	1	+
10	F.G.	75	20	5	–	–	256	251	17	17	+++
11	F.G.	75	20	–	5	–	509	372	34	25	+++
13	F.G.	–	–	100	–	–	No attack				neg
15	F.G. No SO_2	–	–	100	–	–	18	15	1	1	neg
16	F.G. No SO_2	78	21	1	–	–	17	10	1	1	+
18	F.G. No SO_2	78	21	1	–	–	10	9	1	1	neg
17	Helium	78	21	1	–	–	64	37	4	3	neg
19	Helium + 2500 ppm SO_2	78	21	1	–	–	67	59	4	4	neg
21	F.G. + 2500 ppm SO_2	75	20	5	–	–	114	70	7	5	+

(a) Specimen size, 0.8 x 0.75 x 0.125 inch, weight range, 8 to 10 grams.

(b) Based on exposure of 50 hours.

(c) F.G. = flue gas 80% air, 10% CO_2, 10% H_2O, 250 ppm SO_2.

TABLE A-6. LABORATORY CORROSION RESULTS AT 800 F

		Corrosion Mixture, percent					Weight Loss[a], mg		Calculated Corrosion Rate[b], mils per month		
							Specimen		Specimen		Azide Test
Run	Atmosphere	K_2SO_4	Na_2SO_4	NaCl	KCl	Fe_2O_3	1	2	1	2	Results
				A-106 – Grade B Steel							
0	F.G.[c]	–	–	–	–	–	9	–	1	–	neg.
8	F.G.	79	21	–	–	–	18	18	1	1	+
4	F.G.	58	16	1	–	25	47	44	3	3	+
6	F.G.	78	21	1	–	–	69	99	5	7	+
9	F.G.	75	20	5	–	–	264	264	18	18	++
12	F.G.	75	20	–	5	–	98	110	7	7	++
14	F.G.	–	–	100	–	–	34	77	2	5	+++
				A 213 – Grade T11 Steel							
0	F.G.	–	–	–	–	–	8	–	1	–	neg.
8	F.G.	79	21	–	–	–	9	9	1	1	+
4	F.G.	58	16	1	–	25	14	24	1	2	+
6	F.G.	78	21	1	–	–	37	34	3	2	+
9	F.G.	75	20	5	–	–	164	273	11	18	++
12	F.G.	75	20	–	5	–	233	152	15	10	++
14	F.G.	–	–	100	–	–	49	62	3	1	+++
				Type 321 Stainless Steel							
0	F.G.	–	–	–	–	–	No attack		–	–	neg.
8	F.G.	79	21	–	–	–	No attack		–	–	neg.
4	F.G.	58	16	1	–	25	3	4	<1	<1	neg.
6	F.G.	78	21	1	–	–	2	0	<1	0	neg.
9	F.G.	75	20	5	–	–	0	1	0	<1	neg.
12	F.G.	75	20	–	5	–	0	2	0	<1	neg.
14	F.G.	–	–	100	–	–	No attack		0	0	neg.

(a) Specimen size, 0.8 x 0.75 x 0.125 inch; weight range, 8 to 10 grams.

(b) Based on an exposure of 50 hours.

(c) F.G. = flue gas 80% air, 10% CO_2, 10% H_2O, 250 ppm SO_2.

TABLE A-7. LABORATORY CORROSION RESULTS FOR A-106 - GRADE B STEEL AT 600 F

Run	Addition to Atmosphere of 80% Air, 10% CO_2, 10% H_2O			Corrosion Mixture, percent									Weight Loss[a], mg		Calculated Corrosion Rate[b], mils per month		Azide Test Results	Physical State
	SO_2, ppm	HCl, ppm	HCOOH, ppm	K_2SO_4	Na_2SO_4	$K_2S_2O_7$	$KHSO_4$	NaCl	$ZnCl_2$	ZnO	$PbCl_2$	Other	Specimen 1	Specimen 2	Specimen 1	Specimen 2		
35	2.5×10^2	2×10^3	-	-	-	-	-	-	-	-	-	-	17	16	1	1	neg.	-
42	2.5×10^2	2×10^3	2×10^2	-	-	-	-	-	-	-	-	-	17	9	1	<1	neg.	-
24	2.5×10^2	2×10^3	-	75	20	-	-	5	-	-	-	-	0	3	0	<0.5	?	Agglom.
45	2.5×10^2	2×10^3	2×10^2	75	20	-	-	5	-	-	-	-	47	39	4	3	neg.	Agglom.
47	2.5×10^2	2×10^3	10^4	75	20	-	-	5	-	-	-	-	6	4	<0.5	<0.5	?	Agglom.
25	2.5×10^2	2×10^3	-	71	19	-	-	5	-	-	-	5 $ZnSO_4$	2	3	<0.5	<0.5	neg.	Agglom.
26	2.5×10^2	2×10^3	-	71	19	-	-	5	-	-	-	5 $PbSO_4$	7	6	<0.5	<0.5	neg.	Agglom.
27	2.5×10^2	2×10^3	-	71	19	-	-	5	-	5	-	-	12	28	<1	2	++	Caked
29	2.5×10^2	2×10^3	-	71	19	-	-	5	5	-	-	-	131	121	9	8	+++	Caked
43	2.5×10^2	2×10^3	2×10^2	71	19	-	-	5	5	-	-	-	114	121	8	8	+++	Caked
31	2.5×10^2	2×10^3	-	63	17	-	-	5	15	-	-	-	45	65	3	4	+++	Caked
32	2.5×10^2	2×10^3	-	75	20	-	-	-	5	-	-	-	83	95	6	6	++	Caked
33	2.5×10^2	2×10^3	-	71	19	-	-	5	-	-	-	5 Carbon	10	6	<1	<1	+	Powdery
34	2.5×10^2	2×10^3	-	67	18	-	-	5	5	-	-	5 Carbon	92	67	6	4	++++	Caked
37	2.5×10^2	2×10^3	-	67	18	5	-	5	5	-	-	-	81	66	5	4	++++	Caked
53	2.5×10^2	2×10^3	-	71	-	-	-	5	5	-	-	19 $ZnSO_4$	54	50	4	3	+	Agglom.
54	2.5×10^2	2×10^3	-	50	-	-	-	5	30	-	15	-	66	63	4	4	+++	Fused
56	2.5×10^2	2×10^3	-	50	-	-	-	5	15	-	-	30 KH_2PO_4	39	52	3	3	++	Fused
59	2.5×10^2	2×10^3	-	-	-	-	90	5	5	-	-	-	333	293	22	19	+++	Fused
38	2.5×10^2	2×10^3	-	75	20	-	-	-	-	-	-	5 $FeCl_3$	20	16	1	1	+	Caked
39	2.5×10^2	2×10^3	-	75	20	-	-	-	-	-	-	5 $FeCl_2$	16	14	1	1	++	Caked
40	2.5×10^2	2×10^3	-	-	-	50	-	-	-	10	-	10 CaO, 30 Al_2O_3	28	32	2	2	+++	Caked
49	2.5×10^2	2×10^3	-	75	20	-	-	-	-	-	-	5 PbO	20	22	1	2	neg.	Agglom.
51	2.5×10^2	2×10^3	-	63	17	-	-	-	-	-	-	20 PbO	28	31	2	2	?	Agglom.
BDA[c]	Pure HCl Only		-	-	-	-	-	-	-	-	-	-	-	-	5	-	-	-
22	2.5×10^2	-	-	75	20	-	-	5	-	-	-	-	10	5	<1	<1	+	Agglom.
23	2.5×10^2	-	-	71	19	-	-	5	-	-	-	5 $ZnSO_4$	0	2	0	<0.5	neg.	Agglom.
30	2.5×10^2	-	-	71	19	5	-	5	-	-	-	-	29	25	2	2	+	Caked
28	2.5×10^2	-	-	-	-	100	-	-	-	-	-	-	366	377	24	25	+++	Fused
36	2.5×10^2	-	-	-	-	95	-	-	5	-	-	-	25	31	2	2	+++	Fused
41	2.5×10^2	-	-	-	-	95	-	-	5	-	-	-	53	59	4	4	+++	Fused
44	2.5×10^2	-	-	-	-	95	-	5	-	-	-	-	438	464	29	31	+++	Fused
46	2.5×10^2	-	-	-	-	65	-	5	-	-	-	30 Fe_2O_3	45	34	3	2	++	Agglom.
48	2.5×10^2	-	-	-	-	-	100	-	-	-	-	-	108	101	7	7	+	Fused
50	2.5×10^2	-	-	-	-	-	95	5	-	-	-	-	467	438	31	29	+++	Fused
52	2.5×10^2	-	-	-	-	-	50	5	-	-	-	30 $ZnSO_4$, 15 PbO	24	19	2	1	+++	Fused
55	2.5×10^2	-	-	-	-	-	50	5	30	-	15	-	150	141	10	9	+++	Part fused
57	2.5×10^2	-	-	-	-	-	90	5	5	-	-	-	328	332	22	22	+++	Fused
58	2.5×10^2	-	-	-	-	-	80	10	10	-	-	-	180	175	12	12	+++	Fused

(a) Specimen size, 0.8 x 0.75 x 0.125 inch, weight range, 8 to 10 grams.

(b) Based on an exposure of 50 hours.

(c) Brown, DeLong, Auld data.

TABLE A-8. LABORATORY CORROSION RESULTS FOR A-216 – GRADE T11 STEEL AT 600 F

Run	Addition to Atmosphere of 80% Air, 10% CO_2, 10% H_2O			Corrosion Mixture, percent									Weight Loss(a), mg		Calculated Corrosion Rate(b), mils per month		Azide Test Results	Physical State
	SO_2, ppm	HCl, ppm	HCOOH ppm	K_2SO_4	Na_2SO_4	$K_2S_2O_7$	$KHSO_4$	NaCl	$ZnCl_2$	ZnO	$PbCl_2$	Other	Specimen 1	Specimen 2	Specimen 1	Specimen 2		
35	2.5×10^2	2×10^3	–	–	–	–	–	–	–	–	–	–	1	6	<0.5	<0.5	?	–
42	2.5×10^2	2×10^3	2×10^2	–	–	–	–	–	–	–	–	–	11	6	1	1	++	–
24	2.5×10^2	2×10^3	–	75	20	–	–	5	–	–	–	–	0	0	0	0	?	Agglom.
45	2.5×10^2	2×10^3	2×10^2	75	20	–	–	5	–	–	–	–	10	15	1	1	?	Agglom.
47	2.5×10^2	2×10^3	10^4	75	20	–	–	5	–	–	–	–	25	32	2	2	neg.	Agglom.
25	2.5×10^2	2×10^3	–	71	19	–	–	5	–	–	–	5 $ZnSO_4$	0	0	0	0	neg.	Agglom.
26	2.5×10^2	2×10^3	–	71	19	–	–	5	–	–	–	5 $PbSO_4$	4	4	<0.5	<0.5	neg.	Agglom.
27	2.5×10^2	2×10^3	–	71	19	–	–	5	–	5	–	–	26	18	2	1	+	Caked
29	2.5×10^2	2×10^3	–	71	19	–	–	5	5	–	–	–	93	105	6	7	+++	Caked
43	2.5×10^2	2×10^3	2×10^2	71	19	–	–	5	5	–	–	–	113	105	8	7	+++	Caked
31	2.5×10^2	2×10^3	–	63	17	–	–	5	15	–	–	–	98	63	7	4	+++	Caked
32	2.5×10^2	2×10^3	–	75	20	–	–	–	5	–	–	–	77	63	5	4	++	Caked
33	2.5×10^2	2×10^3	–	71	19	–	–	5	–	–	–	5 Carbon	5	6	<0.5	<0.5	neg.	Powdery
34	2.5×10^2	2×10^3	–	67	18	–	–	5	5	–	–	5 Carbon	40	26	3	2	++	Caked
37	2.5×10^2	2×10^3	–	67	18	5	–	5	5	–	–	–	57	60	4	4	+++	Caked
53	2.5×10^2	2×10^3	–	71	–	–	–	5	5	–	–	19 $ZnSO_4$	23	39	2	3	+	Agglom.
54	2.5×10^2	2×10^3	–	50	–	–	–	5	30	–	15	–	56	30	4	2	+++	Fused
56	2.5×10^2	2×10^3	–	50	–	–	–	5	15	–	–	30 KH_2PO_4	40	39	3	3	++	Fused
59	2.5×10^2	2×10^3	–	–	–	–	90	5	5	–	–	–	375	308	25	20	+++	Fused
38	2.5×10^2	2×10^3	–	75	20	–	–	–	–	–	–	5 $FeCl_3$	37	28	2	2	++	Caked
39	2.5×10^2	2×10^3	–	75	20	–	–	–	–	–	–	5 $FeCl_2$	27	23	2	2	++	Caked
40	2.5×10^2	2×10^3	–	–	–	50	–	–	–	10	–	10 CaO 30 Al_2O_3	26	16	2	1	+++	Caked
49	2.5×10^2	2×10^3	–	75	20	–	–	–	–	–	–	5 PbO	50	59	3	4	neg.	Agglom.
51	2.5×10^2	2×10^3	–	63	17	–	–	–	–	–	–	20 PbO	[illegible]	13	2	1	?	Agglom.
22	2.5×10^2	–	–	75	20	–	–	5	–	–	–	–	5	5	<0.5	<0.5	neg.	Agglom.
23	2.5×10^2	–	–	71	19	–	–	5	–	–	–	5 $ZnSO_4$	0	0	0	0	?	Agglom.
30	2.5×10^2	–	–	71	19	5	–	5	–	–	–	–	36	26	2	2	+	Caked
28	2.5×10^2	–	–	–	–	100	–	–	–	–	–	–	440	503	29	33	+++	Fused
36	2.5×10^2	–	–	–	–	95	–	–	5	–	–	–	43	32	3	2	+++	Fused
41	2.5×10^2	–	–	–	–	95	–	–	5	–	–	–	83	84	6	6	++	Fused
44	2.5×10^2	–	–	–	–	95	–	5	–	–	–	–	416	465	27	31	+++	Fused
46	2.5×10^2	–	–	–	–	65	–	5	–	–	–	30 Fe_2O_3	17	26	1	2	++	Agglom.
48	2.5×10^2	–	–	–	–	–	100	–	–	–	–	–	113	139	8	9	+++	Fused
50	2.5×10^2	–	–	–	–	–	95	5	–	–	–	–	410	376	27	25	+++	Fused
52	2.5×10^2	–	–	–	–	–	50	5	–	–	–	30 $ZnSO_4$, 15 PbO	10	9	<1	<1	+++	Fused
55	2.5×10^2	–	–	–	–	–	50	5	30	–	15	–	58	114	4	8	+++	Part fused
57	2.5×10^2	–	–	–	–	–	90	5	5	–	–	–	381	316	25	21	+++	Fused
58	2.5×10^2	–	–	–	–	–	80	10	10	–	–	–	198	184	13	12	+++	Fused

(a) Specimen size, 0.8 x 0.75 x 0.125 inch; weight range, 8 to 10 grams.

(b) Based on an exposure of 50 hours.

TABLE A-9. LABORATORY CORROSION RESULTS FOR TYPE 321 STAINLESS STEEL AT 600 F

Run	Addition to Atmosphere of 80% Air, 10% CO_2, 10% H_2O			Corrosion Mixture, percent									Weight Loss[a], mg		Calculated Corrosion Rate[b], mils per month		Azide Test Results	Physical State
	SO_2, ppm	HCl, ppm	HCOOH ppm	K_2SO_4	Na_2SO_4	$K_2S_2O_7$	$KHSO_4$	NaCl	$ZnCl_2$	ZnO	$PbCl_2$	Other	Specimen 1	Specimen 2	Specimen 1	Specimen 2		
35	2.5×10^2	2×10^3	–	–	–	–	–	–	–	–	–	–	3	6	0.5	0.5	...	–
42	2.5×10^2	2×10^3	2×10^2	–	–	–	–	–	–	–	–	–	0	0	0	0	neg.	–
24	2.5×10^2	2×10^3	–	75	20	–	–	5	–	–	–	–	0	0	0	0	neg.	Agglom.
45	2.5×10^2	2×10^3	2×10^2	75	20	–	–	5	–	–	–	–	0	0	0	0	neg.	Agglom.
47	2.5×10^2	2×10^3	10^4	75	20	–	–	5	–	–	–	–	0	0	0	0	neg.	Agglom.
25	2.5×10^2	2×10^3	–	71	19	–	–	5	–	–	–	5 $ZnSO_4$	0	0	0	0	neg.	Agglom.
26	2.5×10^2	2×10^3	–	71	19	–	–	5	–	–	–	5 $PbSO_4$	0	0	0	0	neg.	Agglom.
27	2.5×10^2	2×10^3	–	71	19	–	–	5	–	5	–	–	0	7	0	0.5	..	Caked
29	2.5×10^2	2×10^3	–	71	19	–	–	5	5	–	–	–	0	0	0	0	neg.	Caked
43	2.5×10^2	2×10^3	2×10^2	71	19	–	–	5	5	–	–	–	1	0	<0.5	0	.	Caked
31	2.5×10^2	2×10^3	–	63	17	–	–	5	15	–	–	–	25	26	2	2	...	Caked
32	2.5×10^2	2×10^3	–	75	20	–	–	–	5	–	–	–	0	0	0	0	neg	Caked
33	2.5×10^2	2×10^3	–	71	19	–	–	5	–	–	–	5 Carbon	0	0	0	0	neg.	Powdery
34	2.5×10^2	2×10^3	–	67	18	–	–	5	5	–	–	5 Carbon	0	0	0	0	neg.	Caked
37	2.5×10^2	2×10^3	–	67	18	5	–	5	5	–	–	–	4	7	<0.5	<0.5	...	Caked
53	2.5×10^2	2×10^3	–	71	–	–	–	5	5	–	–	19 $ZnSO_4$	9	9	<0.5	<0.5	.	Agglom.
54	2.5×10^2	2×10^3	–	50	–	–	–	5	30	–	15	–	0	0	0	0	...	Fused
56	2.5×10^2	2×10^3	–	50	–	–	–	5	15	–	–	30 KH_2PO_4	14	20	1	1	.	Fused
59	2.5×10^2	2×10^3	–	–	–	–	90	5	5	–	–	–	285	278	19	18	..	Fused
38	2.5×10^2	2×10^3	–	75	20	–	–	–	–	–	–	5 $FeCl_3$	0	0	0	0	?	Caked
39	2.5×10^2	2×10^3	–	75	20	–	–	–	–	–	–	5 $FeCl_2$	1	2	0.5	0.5	+	Caked
40	2.5×10^2	2×10^3	–	–	–	50	–	–	–	10	–	10 CaO. 30 Al_2O_3	0	0	0	0	.	Caked
49	2.5×10^2	2×10^3	–	75	20	–	–	–	–	–	–	5 PbO	0	0	0	0	neg.	Agglom.
51	2.5×10^2	2×10^3	–	63	17	–	–	–	–	–	–	20 PbO	0	0	0	0	neg	Agglom.
22	2.5×10^2	–	–	75	20	–	–	5	–	–	–	–	0	0	0	0	neg.	Agglom.
23	2.5×10^2	–	–	71	19	–	–	5	–	–	–	5 $ZnSO_4$	0	0	0	0	neg.	Agglom.
30	2.5×10^2	–	–	71	19	5	–	5	–	–	–	–	5	4	<1	<1	?	Caked
28	2.5×10^2	–	–	–	–	100	–	–	–	–	–	–	410	398	27	26	+++	Fused
36	2.5×10^2	–	–	–	–	95	–	–	5	–	–	–	395	280	26	19	+++	Fused
41	2.5×10^2	–	–	–	–	95	–	–	5	–	–	–	438	391	29	26	+++	Fused
44	2.5×10^2	–	–	–	–	95	–	5	–	–	–	–	646	560	43	37	++	Fused
46	2.5×10^2	–	–	–	–	65		5	–	–	–	30 Fe_2O_3	0	0	0	0	neg.	Agglom.
48	2.5×10^2	–	–	–	–	–	100	–	–	–	–	–	295	250	19	17	+	Fused
50	2.5×10^2	–	–	–	–	–	95	5	–	–	–	–	621	636	41	42	+++	Fused
52	2.5×10^2	–	–	–	–	–	50	5	–	–	–	30 $ZnSO_4$. 15 PbO	17	15	1	1	neg.	Fused
55	2.5×10^2	–	–	–	–	–	50	5	30	–	15	–	36	28	2	2	++	Part fused
57	2.5×10^2	–	–	–	–	–	90	5	5	–	–	–	310	266	21	18	..	Fused
58	2.5×10^2	–	–	–	–	–	80	10	10	–	–	–	193	180	13	12	+	Fused

(a) Specimen size, 0.8 x 0.75 x 0.125 inch; weight range, 8 to 10 grams.

(b) Based on an exposure of 50 hours.

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